Spring 2016

APPLICATION OF QUAL2K MODEL TO MACROPHYTE RICH SILVER BOW CREEK

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by

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A thesis submitted in partial fulfillment of the requirements for the degree of

Master of Science in Environmental Engineering

Montana Tech

2016

Abstract

Silver Bow Creek (SBC, Blacktail Creek to Warm Springs Creek) is a small urbanized stream in western Montana (MT) identified as impaired for nitrate, total nitrogen and total phosphorus on the 2014 303(d) list. Enrichment of SBC occurs primarily from a single municipal point source that results in excessive primary production, macrophyte growth, large diel water-quality swings, and nightly hypoxic conditions that likely impair aquatic life uses. The objective of this study is to apply QUAL2K (a surface water-quality model) to a 5.6 km long reach of SBC to predict in-stream dissolved oxygen (DO) concentrations under different nutrient loading scenarios. Using the developed model, existing and future nutrient loads from the wastewater treatment plant will be evaluated to determine the effect on longitudinal DO. Data collection in support of model development on SBC has included (a) continuous DO, conductivity, temperature and pH measurement using YSI Exo Sondes and sampling of (b) nutrients, suspended solids, and alkalinity at four locations. Nearby climatic forcing data were obtained from Bert Mooney Airport, Butte, MT. Preliminary model runs have produced poor results, however, due in part to a large macrophyte biomass present in SBC. Photosynthesis during the day drives DO well above saturation and contributes to hypoxic conditions at night through respiration. Currently QUAL2K does not support macrophytes, so approximations were made using closely spaced point sources with diurnal variation to accommodate the macrophyte DO source/sink. Using these approximations a theoretical total maximum daily load for nutrients was estimated so that dissolved oxygen concentrations are above 4 mg/L. A 70% reduction in nutrient concentrations is required to meet the 4 mg/L dissolved oxygen minimum.

Keywords: Surface Water Quality, Modeling, QUAL2K, Macrophytes, Nutrient Loading, Dissolved Oxygen

Dedication

I wish to thank my mother, father, and brother for all their love and support.

Acknowledgements

I would like to acknowledge the following people who have made valuable contributions to this thesis:

Dr. Raja Nagisetty**
Montana Tech of the University of Montana
Department of Environmental Engineering

Dr. Bill Drury*
Montana Tech of the University of Montana
Department of Environmental Engineering

Dr. Kyle Flynn*
Montana Department of Environmental Quality

Dr. Kahlid Miah*
Montana Tech of the University of Montana
Department of Geophysical Engineering

Dr. Kumar Ganesan
Montana Tech of the University of Montana
Department of Environmental Engineering

Jeanne Larson
Montana Tech of the University of Montana
Department of Environmental Engineering

Dr. Alysia Cox
Montana Tech of the University of Montana
Department of Chemistry

Garrett Craig
Montana Tech of the University of Montana
Department of Environmental Engineering

Sam Hutcheson
Montana Tech of the University of Montana
Department of Environmental Engineering

Derek McDowell
Sampling Support Team

Gary Wyss
Montana Tech of the University of Montana
Center for Advanced Mineral and Metallurgical Processing

Frank Shields
Butte-Silver Bow Wastewater Treatment Plant

Ted Duaime
Montana Bureau of Mines and Geology

Montana Tech
For the seed grant to Raja Nagisetty for financial support

**Committee Chair

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1. Introduction

Nitrogen and phosphorus are essential nutrients that support stream ecosystems, however, when present in excess quantities may lead to eutrophication of water bodies. Eutrophication refers to the over-enrichment of surface waters by nutrients that result in excessive aquatic plant or algal growth. It may cause a variety of undesirable water quality changes such as human health concerns, diminished aquatic communities, and development of hypoxia or dead zones. Hypoxia refers to the water bodies with dissolved oxygen (DO) levels less than the necessary concentrations to sustain most animal life and result in fish kills. Further concerns of eutrophication include loss of recreational amenity, reduced property values, tourism losses, and increased drinking water treatment costs. Nutrient impairment is a major concern for many streams in the USA.

The main purpose of this project was to develop an initial QUAL2K model to predict the effects of various parameters on the downstream water quality. Wherever possible, measured data from the studied reach was used. The reach begins below the Butte-Silver Bow Waste Water Treatment Plant (WWTP), which is located on Silver Bow Creek. This thesis describes the methods used to obtain the data and how it was incorporated into the model. The model was used to predict the total daily maximum load (TMDL) of nutrients that could be discharged into the stream without creating hypoxic zones within the modeled reach. In order to prevent hypoxic conditions in stream a theoretical TMDL was calculated based off of the results from the model. This project set up the basic groundwork for future modeling of Silver Bow Creek and methods to improve the QUAL2K model, specifically with respect to its current limitations regarding macrophytes.

1.1. Total Maximum Daily Load (TMDL)

TMDL is a regulatory term that describes the amount of pollutant that can enter a water body per day for it to meet the water quality standards for that pollutant. They are widely used by the United States Environmental Protection Agency to regulate pollutant discharges. TMDLs are written to reduce pollutant loadings such that designated uses are achieved for an impaired water body. An application of a hypothetical TMDL to Silver Bow Creek could prevent hypoxic conditions from occurring downstream of the WWTP. Silver Bow creek is already regulated by TMDLs for some pollutants (MT DEQ, 2011).

The designated use is based on the various ways a particular waterbody can be used by people, wildlife, and livestock. This might include habitat for fish and waterfowl, recreation, or agricultural and industrial purposes (MT DEQ, 2016). Silver Bow Creek has a Class I designated use (Montana Department of Environmental Quality, 2016). A Class-I designation means “the goal of the State of Montana is to have these waters fully support the following uses: drinking, culinary, and food processing purposes after conventional treatment; bathing, swimming, and recreation; growth and propagation of fishes and associated aquatic life, waterfowl, and furbearers; and agricultural and industrial water supply” (MT DEQ, 2012). Silver Bow Creek is headwaters to Clark Fork River, which is listed as a B-1 classification (Montana Department of Environmental Quality, 2016). A B-1 classification means the water should be “suitable for drinking, culinary, and food processing purposes after conventional treatment; bathing, swimming, and recreation; growth and propagation of salmonid fishes and associated aquatic life, waterfowl, and furbearers; and agricultural and industrial water supply” (MT DEQ, 2012).

1.2. Silver Bow Creek

Silver Bow Creek covers about 40 miles of stream and streamside habitat with early sections running through urban Butte, and eventually flowing into the Clark Fork River (Butte CTEC, 2016). It is also one of multiple Superfund sites in the Upper Clark Fork River Basin. Since the late 1800's mining wastes were dumped into and near Silver Bow Creek, which contaminated soil, groundwater, and surface water with heavy metals. The cleanup of Silver Bow Creek has been ongoing since 1999 as part of a Superfund remedial action coordinated by the Montana Department of Environmental Quality (DEQ) (MT DEQ, 2012). Recently Silver Bow Creek has seen the return of westslope cutthroat trout to the stream, prompting the return of fishing regulations to Silver Bow Creek (MT FWP, 2012). When calculating the TMDLs for Silver Bow Creek the more strict B-1 designation of the Clark Fork River was used to protect the newly returned westslope cutthroat.

A previous study in the summers of 2007 and 2008 showed that Silver Bow Creek contained a large hypoxic zone below the local WWTP outfall (Gammons, Babcock, Parker, & Poulson, 2011). This study characterized a 2-km long reach that was marked by nightly hypoxia, large diel cycles of dissolved oxygen, and extreme growth of macrophytes.

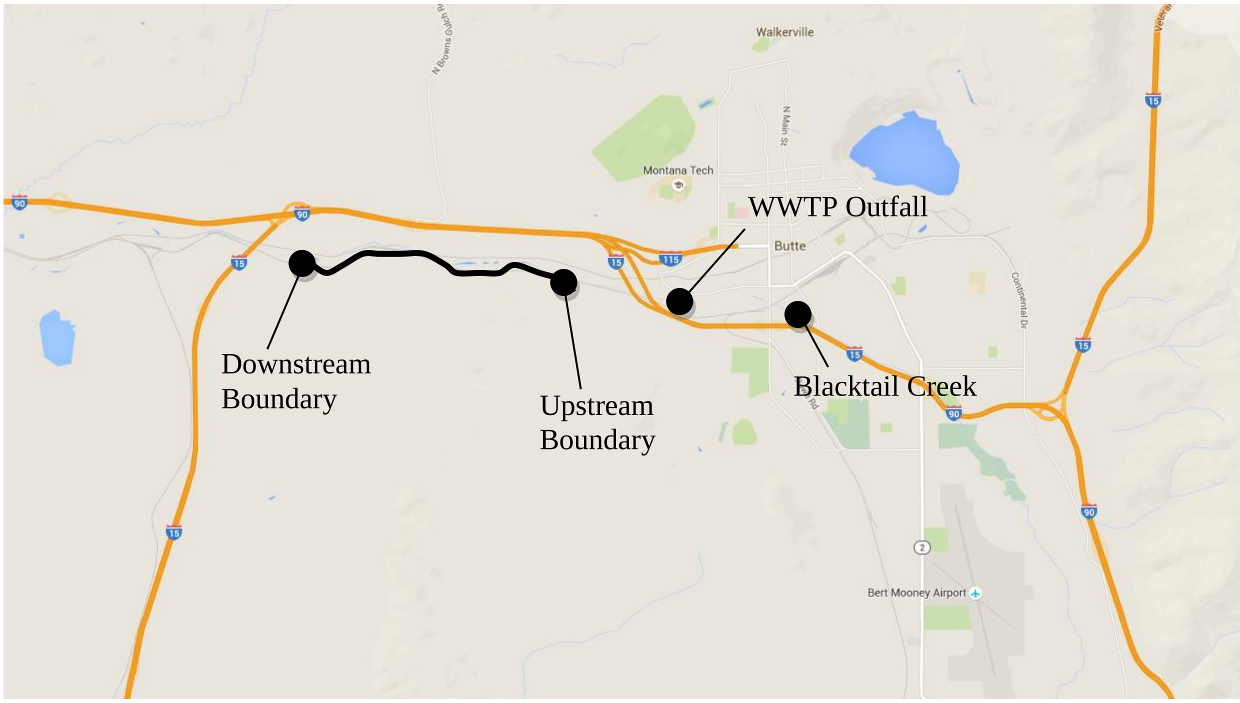

Figure 1: Site Map of Silver Bow Creek Study Reach

At the time of the writing of this thesis, the Butte-Siler Bow WWTP was discharging a large concentration of nutrients into Silver Bow Creek. The WWTP was under construction to add a membrane bio-reactor treatment system, which should reduce the nutrient effluent. The form of nitrogen in the effluent was principally ammonia and now will be converted to more oxidized forms (e.g., nitrate). Additionally, a large amount of bioavailable of phosphorus is also discharged into the stream. The large excess of available nutrients result in large macrophyte blooms that inundated the stream for several kilometers. Macrophytes were present throughout the studied reach, and the macrophyte density was observed to be higher at the upstream end than the downstream end of the reach.

While the WWTP has a MPDES permit, the stream has not been modeled to ensure that the effluent will not impair the stream. One of the major goals of this project was to use the model to predict if the stream would still be impaired after upgrades to the plant have been finished. For the purpose of this project the stream is impaired when it does not meet the designated use dissolved oxygen values. Thus the primary question in this work is “What nutrient loads and concentrations will result in attainment of the designated use of Silver Bow Creek?”

1.3. Macrophytes

Due to enrichment by the WWTP, Silver Bow Creek is inundated by a number of macrophytes, primarily sago pondweed (*Potamogeton pectinatus)*, but also contains some white water buttercup (*Ranunculus aquatilis)*, common duckweed (*Lemna minor)*, and common water moss (*Fontinalis antipyretica)* (Mitman, 2015). The macrophytes partially die off each winter and will grow back over the course of the summer. In July of 2015, macrophytes were a thick mat across bottom of the stream and in most places had grown to the surface of the flowing water.

1.3.1. Dissolved Oxygen

Macrophytes have a significant impact on the dissolved oxygen balance of Silver Bow Creek. During the daytime they photosynthesize, producing more oxygen than is required by the plants for respiration, and adding dissolved oxygen to the stream. The dissolved oxygen at this time can be significantly above atmospheric saturation. At night, macrophytes are unable to photosynthesize but still continue to respire, consuming available oxygen. This is an important factor to why there are nightly hypoxic conditions in the stream as there is a very high demand for dissolved oxygen.

1.3.2. Alkalinity and pH

While nitrogen and phosphorus concentrations are generally the limiting nutrients for plant growth, in some systems aquatic plants can become carbon dioxide (CO_2) limited because of its low diffusivity through water. The way in which water flows over the foliage of the macrophytes forms a relatively thick unstirred layer, also known as a Prandtl Boundary. Water in this layer is not well mixed with the remaining water column and is generally low in dissolved CO_2. Many aquatic species are instead able to fix bicarbonate during photosynthesis to overcome the shortage of dissolved CO_2. The conversion of HCO_3^- to CO_2 is catalyzed by an extracellular carbonic anhydrase, which is closely associated with the cell walls of the outer layer of plants cells. This carbon concentrating mechanism allows the macrophytes to photosynthesize even during peak hours of photosynthesis when there is very low dissolved CO_2 (Lambers, Chapin, & Pons, 2008). As the macrophytes take in bicarbonate there should be a decrease in alkalinity observed downstream, since bicarbonate and alkalinity are related to one another (Huebert).

Equation (1): Bicarbonate System

$$CO_{2(g)} + H_2O \leftrightarrow H_2CO_{3(aq)} \leftrightarrow H^+ + HCO_3{}^-$$

Since alkalinity is directly related to the pH of the stream, as macrophytes fix CO_2 and bicarbonate, it impacts the pH of the stream. As macrophytes photosynthesize during the day they fix carbon dioxide and bicarbonate removing them from the water column, raising the pH and impacting the alkalinity of the stream. At night the macrophytes can continue to respire without photosynthesis, which results in a net output of carbon dioxide during night time hours. This drives the bicarbonate system back in the other direction, creating more bicarbonate and decreasing the pH. It is expected that the pH of the stream is highest in the middle of the day during peak photosynthesis hours, and lowest just before sunrise where the plants switch from primarily respiration to photosynthesizing (Utah State University, 2016).

1.3.3. Nutrients

The nutrients that plants require can be divided into two groups, micronutrients and macronutrients. Micronutrients are required in trace amounts to maintain healthy plant function, like iron, zinc, silica, and manganese. Macronutrients are required in large amounts by plants to grow and compose most of the plants mass, like carbon, nitrogen, and phosphorus. Referring to nutrients in a stream generally means the amount of nitrogen and phosphorus that is available since these are almost always the nutrients that limit plant growth.

Macrophytes are capable of taking in their required nutrients from both their root systems and foliage. In fact macrophytes do not rely solely on roots or foliage to take in any of their required nutrients and are “able to satisfy demand for mineral nutrients by leaf nutrient uptake alone” (Madsen & Cedergreen, 2002). Removal of the roots has no negative impact on the growth rate of the plants. This research also showed that when the macrophytes were whole, the roots in general take in most of the nitrogen, phosphorus, and micronutrient demands, while the foliage takes in most of the calcium, magnesium, sodium, potassium, and sulfate demands. While macrophytes are able to take in nutrients from the soil, it is important to note that they are also capable of taking in a significant amount of nutrients from the water column (Madsen & Cedergreen, 2002). This makes determination of nitrification and denitrification rates more difficult since macrophyte uptake impacts nitrogen and ammonia concentrations. It should be noted that the relative importance of the water column uptake mechanism increases with increasing concentration of nutrient availability (Feijoo, Garcia, Momo, & Toja, 2002). Potentially, the Silver Bow Creek water column could be the primary source of nutrients instead of the sediments.

Even though nitrate and ammonia are the primary sources of nitrogen for macrophytes, they exhibit different rates of uptake. Nitrate is taken in based on light intensity the macrophytes are exposed to, almost stopping intake when it is dark enough, while ammonia is taken in at a pseudo-linear rate based on the concentration of the water around the macrophytes (Nelson, Smith, & Best, 1981). This is likely because ammonia is a more useful form of nitrogen to plants since it is in a more reduced state. The constant uptake of ammonia appears to be a luxury uptake of a more useful nutrient, whenever it is available. Taking in ammonium has been shown to increase the concentration of nitrogen in plants, but not necessarily increase biomass, meaning it is being stored in some manner or being used for something other than growth or for use later when nutrients become scarce (Feijoo, Garcia, Momo, & Toja, 2002).

1.4. QUAL2K

QUAL2K is a widely applied one dimensional, stream or river eutrophication model that is supported by the EPA (United States Environmental Protection Agency, 2009). Originally the model was downloaded from the Washington Department of Ecology website, but small changes were made to use point sources to appropriately account for macrophytes (Washington Department of Ecology, 2016). This model has been used worldwide for total maximum daily load (TMDL) development and numeric nutrient criteria development and extensive regulatory use. Some examples for this are the Pocomoke River in Delaware (Delaware Department of Natural Resources and Environmental Control, 2005), the Colorado River Basin Region in California (Tetra Tech, Inc., 2009), the Peterson Creek here in Montana (PBS&J, 2008), the South Umpqua River (Turner, Pelletier, & Kasper, 2009), and Yellowstone River (Flynn, Suplee, Chapra, & Tao, 2014).

QUAL2K models water quality parameters in one dimension. The model assumes the channel is well-mixed vertically and laterally, and that the flow regime is steady state. It operates on a diel cycle, which accounts for the variations between day and night in the heat budget and water-quality kinetics. Numerical computations are programmed in Fortran 90, while Microsoft Excel is used as the graphical user interface. The model uses an extensive list of inputs to estimate various parameters along the length of a designated reach. Each output gives the predicted daily maximum, minimum, and average values for a specific parameter along the reach for one 24-hour period. The model developed for this project was designed to predict dissolved oxygen concentrations during the critical period, when the temperatures are high and stream flows are low. If the stream is not impaired for dissolved oxygen at this time, it would be reasonable to assume at all other times the stream would not be impaired (Flynn, Chapra, Pelletier, & Tao, 2015).

1.4.1. Macrophyte Limitations

While QUAL2K has inputs to predict the growth and effects of phytoplankton and bottom algae cover, it currently does not have a method to account for macrophytes present in a stream. Macrophytes are plants that have roots in the stream sediments and extend vertically in the water column, sometimes reaching the stream surface. Developing a simple way to account for macrophytes in the stream became one of the key topics of this project once they were discovered to be a key component of the dissolved oxygen balance for the reach selected. Part of what makes macrophytes difficult to model with QUAL2K is that they can take a long time to grow to peak biomass within the stream. Algae and phytoplankton can be modeled for available nutrient concentrations because they grow very quickly in stream. However the macrophyte density in Silver Bow Creek increases over the growing season. The model repeatedly runs the 24-hour input to fully characterize the length of the reach, but this also makes it unsuitable to account for long term macrophyte growth. As different days have different physical parameters it cannot accurately account for the long term growth of macrophytes under varying conditions. This makes modeling future concentrations of contaminants somewhat difficult since macrophyte loading and growth rates are tied to nutrient loading in the stream. Decreasing the nutrients in the stream would naturally decrease the amount of macrophytes that could be supported, and their effects on the water quality. Without some sort of relation of nutrient loading to macrophyte growth then it would be impossible to predict the new maximum macrophyte loading, or effects on water quality (Flynn, Chapra, Pelletier, & Tao, 2015).

Macrophytes can be approximated for in QUAL2K by adding a series of point sources in the “Point Source” tab of the model (Flynn K. , 2015). The idea is to create discrete inputs or outputs of dissolved oxygen at regular intervals with negligible flows to adjust the mass balance of dissolved oxygen in the stream to more closely match observed concentrations. This method will be discussed in greater detail in section *3.9 Macrophyte Compensation*.

2. Methods

In order to develop a QUAL2K model both water quality and atmospheric data are required to account for all parameters that affect the system (e.g., boundary conditions and forcing functions). Nearly all of the water quality data were measured specifically for this project as described later in the methods. The local atmospheric data was obtained from the weather station at the local Bert Mooney Airport.

QUAL2K utilizes spatial and temporal data to create a more complete prediction in the stream. The model requires 24-hours of data to account for temporal changes and daily cycles of inputs. Four sampling locations were used to represent the reach spatially. The upstream boundary, Whiskey Gulch, was chosen because the stream was far enough downstream from the WWTP discharge that the complete mixing of the WWTP effluent and Silver Bow Creek could be assumed. The next sampling location, noted as Beaver Dam, was located just below the final beaver dam on the reach. This sampling location was to determine if the beaver dams significantly impacted the water quality. The third location was near a walking trail in Rocker. This site was chosen for its spacing between the beaver dam and downstream boundary, and its accessibility. The downstream boundary was chosen because of the decreasing presence of macrophytes seen growing in the stream.

Table I Site Distance from Downstream Boundary

Sampling Site	Distance from Downstream Boundary (km)
Whiskey Gulch (Upstream Boundary)	5.83
Beaver Dam	4.76
Rocker	3.01
I-15 (Downstream Boundary)	0

2.1. Field Work

One sampling even on August 22, 2015 was used to develop the model, taking samples at four locations along Silver Bow Creek at four times simultaneously. Water quality data is necessary for at least the upstream and downstream boundaries, and the data from other locations are used to estimate rate constants and compare to the model outputs (i.e. calibration).

2.1.1. Sondes

Four sondes were used for continuous monitoring in this project, with their locations noted in Figure 2. Two YSI EXO II Sondes were used to collect continuous water quality data at the upstream and downstream boundaries of the model. Two Hydrolab sondes were also placed along the stream; one after the beaver ponds and the other near an entrance to the local walking trail in Rocker, MT. The sondes were used to continuously monitor temperature, conductivity, dissolved oxygen, and pH along the reach.

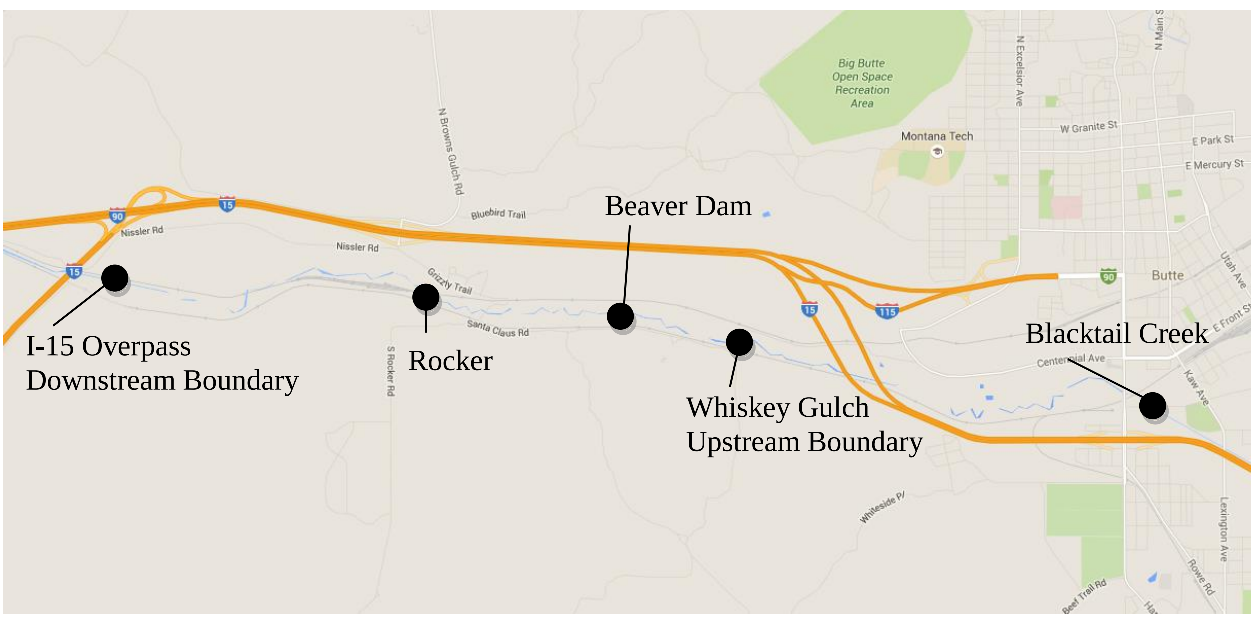

Figure 2: Sonde Site Map

Sondes were set in the main flow path of the stream inside of PVC housings with holes drilled to allow sufficient water flow through them, but prevent any movement or damage to the sondes. Over time the housings would collect large masses of sticks, branches, and loose macrophytes that were flowing downstream. When collecting data for the model it was removed several times during the day to prevent any inconsistencies that the debris might have caused.

The sondes were calibrated according to their respective manuals. Most calibrations involved a two or three point standardization. All sondes were calibrated at the same time, one day before sampling events. During the sampling event for model development an additional sonde was used to check all sonde results side by side.

2.1.2. Grab Samples

Grab samples were obtained from the center flow of the stream, at about 2/3 of the depth of the water column. Samples were taken immediately downstream of the recording sondes to ensure consistency. Sample bottles were cleaned with 10% hydrochloric acid before use. When sampling, the bottles were rinsed three times with stream water, collecting from the upstream side and discharging in the downstream direction. After a sample was collected it was labeled and immediately chilled.

2.2. Lab Analysis

The chilled samples were tested for alkalinity, detritus, inorganic solids, and orthophosphate as soon as possible since acid preserving would have ruined these parameters. Once enough of each sample was separated for the immediate testing the remainder of the sample was preserved with sulfuric acid to below a pH of 2. The samples were neutralized as necessary for the remaining analysis of nitrate, ammonia, organic nitrogen, orthophosphate, and total phosphate (United States EPA, 1962).

2.2.1. Alkalinity

50 mL samples were measured into a beaker. A stir bar was added to completely mix the solution during the titration process. Phenolphthalein was added as a visual aid to determine when the titration was nearing completion and freshly calibrated pH probe was used to determine when the solution had reached a final pH of 4.5. The samples were titrated with a solution of 0.02 normal sulfuric acid in a burette, recording the initial and final mL values to determine how much was added for each test. Total alkalinity of the samples was calculated by the following equation (Snoeyink & Jenkins, 1980).

Equation (2): Total Alkalinity

$$Alkalinity = \frac{\left(V_a * N_a * 50{,}000\,\frac{mg\ CaCO_3}{eq}\right)}{V_s}$$

V_a = Volume of acid used to reach pH 4.5 (mL)
N_a = Normality of acid (eq/L)
V_s = Volume of sample (mL)

2.2.2. Inorganic Solids and Detritus

One liter samples of water were filtered through filters of known mass. These were then dried at 100°C for 12 hours in a drying oven. The samples were then cooled in a desiccator and weighed again. Next the filters were transferred to a furnace at 550°C for 1 hour. They were then allowed to cool to room temperature in a desiccator and weighed again for the final time. The inorganic solids and detritus values were calculated using the following equations.

Equation (3): Inorganic Solids

$$C_s = \frac{M_3 - M_1}{V_s}$$

C_s = Concentration of inorganic solids (g/L)
M_1 = Initial mass of filter paper (g)
M_3 = Mass of filter paper after furnace (g)
V_s = Volume of sample filtered (L)

Equation (4): Detritus

$$C_d = \frac{M_2 - M_3}{V_s}$$

C_d = Concentration of detritus (g/L)
M_2 = Mass of filter paper after filtering and drying (g)
M_3 = Mass of filter paper after furnace (g)
V_s = Volume of sample filtered (L)

2.2.3. Nutrients

A flow injection analyzer (FIA) was used to determine nutrient concentrations. A one in ten dilution was required for all the samples since the nutrients were present at such high concentrations in stream. EPA approved methods were used to determine the ammonia, nitrate and nitrite, total Kjeldhal nitrogen, organic phosphorus, and orthophosphate concentrations that were used for the model. The organic nitrogen used in the model is equal to total Kjeldhal nitrogen minus ammonia.

Table II: Nutrient Analysis EPA Methods

Nutrient	EPA Test Method
Orthophosphate	365.1
Nitrate + Nitrite	353.2
Ammonia	350.1
Total Phosphorus	365.4
Total Kjeldahl Nitrogen	351.2

2.3. Sediment Oxygen Demand

In order to estimate the sediment oxygen demand for the model, sediment samples were taken from Silver Bow Creek. Ideally a core sample several inches deep would provide the most accurate results, but the rocky base of Silver Bow Creek prevented the corer from collecting a sample. Instead a sample tube was filled with 6-8 inches of sediment and covered with stream water to fill the remaining space. An identical sample tube was filled with stream water to be used as a blank core to determine the water column oxygen demand. Cores were stored on ice during transport to an incubator in the lab set to 14°C, the average temperature of the water during model testing. Initial and final dissolved oxygen values were recorded for the blank tube while the core was monitored continuously over a 24-hour period. The change in dissolved oxygen in the blank tube was subtracted from the change in the core tube to account for the water column oxygen demand. The following equation was then used to correct the units for the model.

Equation (5): Sediment Oxygen Demand

$$SOD = (dC_c - dC_w) * H$$

SOD = Sediment oxygen demand ($g/m^2/d$)
dC_c = Change in dissolved oxygen concentration of sediment core (mg/L/d or $g/m^3/d$)
dC_w = Change in dissolved oxygen concentration in water column blank (mg/L/d)
H = Height of water column above sediment core or in blank (meters)

QUAL2K requires model input parameters at 20°C, meaning the rates estimated at the stream temperature have to be adjusted to 20°C for model inputs. The calculated SOD was converted to the 20°C value by using the Arrhenius Equation, listed below (Crittenden, Trussell, Hand, Howe, & Tchobanoglous, 2005).

Equation (6): Arrhenius Equation

$$k_T = k_{20}(\theta^{T-20})$$

k_T = Rate constant at temperature T (day^{-1})
k_{20} = Rate constant at 20°C (day^{-1})
θ = Rate adjustment constant (unitless)
T = Temperature (°C)

Table III: θ Values for Arrhenius Equations

Parameter	θ Value
CBOD	1.047
Nitrification	1.07
Denitrification	1.07

2.4. Bert Mooney Airport Meteorological Data

The local air temperature, dew point temperature, wind speed, and cloud cover data were all downloaded from the Bert Mooney Airport weather data web page (National Weather Service, 2015), which is located only 5 miles away from the sampled reach and is about the same elevation. There could be some small discrepancies in data since the airport's weather station is not located directly next to a water source, but it is within the Silver Bow Creek drainage basin.

3. Model Development

All of the input data for the QUAL2K model is entered into a Microsoft Excel file, which is used as a graphical user interface. FORTRAN is used to calculate the model values based on the data input in the Excel file. There are a multitude of tabs in the Excel file each relating to different model inputs and outputs. The first set of blue tabs are for the data used to build the model. Observed values along the reach are entered in the yellow tabs. The green tabs are the model output values. The purple tabs are the model outputs in graphical form. The second set of blue tabs are used to show diel variations of parameters.

3.1. Headwater

The headwater tab is used to input the upstream boundary data for the stream reach to be modeled. QUAL2K has the ability to model several streams in a watershed as they join and mix with one another. The primary stream is designated as the “Headwater 0” or the Mainstem. Each tributary is designated as such “Headwater 1” with increasing numbers for each new reach. All of the entered reaches will be modeled and can be selected for viewing output data after the model has run. The Headwater tab requires hourly data for each of the following sub-headings.

For the discrete data, four grab samples from four sampling locations were used to provide nutrient, solids, and alkalinity. Previous sample runs have shown limited diel variation in nutrient loading from the WWTP. Limited resources prevented sampling for 24-hour nutrient data for the model date, so the input values were averaged to calculate the upstream boundary concentrations. This averaged value was used for each hour of the model. While this means the model will slightly differ from observed results, especially the daily max and min values, it should still provide a close approximation. Future projects with more manpower and equipment could sample more frequently to improve the accuracy. 24-hour data recorded by sondes and the local weather station was used wherever available.

3.1.1. Temperature

Water temperatures recorded by the sondes were entered into QUAL2K for each hour of the day and then computes temperature for the remaining parts of the modeled reach. Temperature affects the rate constants used by the model such as nitrification, denitrification, and gas transfer rates. Sondes were used to record in stream temperature data and an example of the upstream and downstream boundary data are shown in Figure 3.

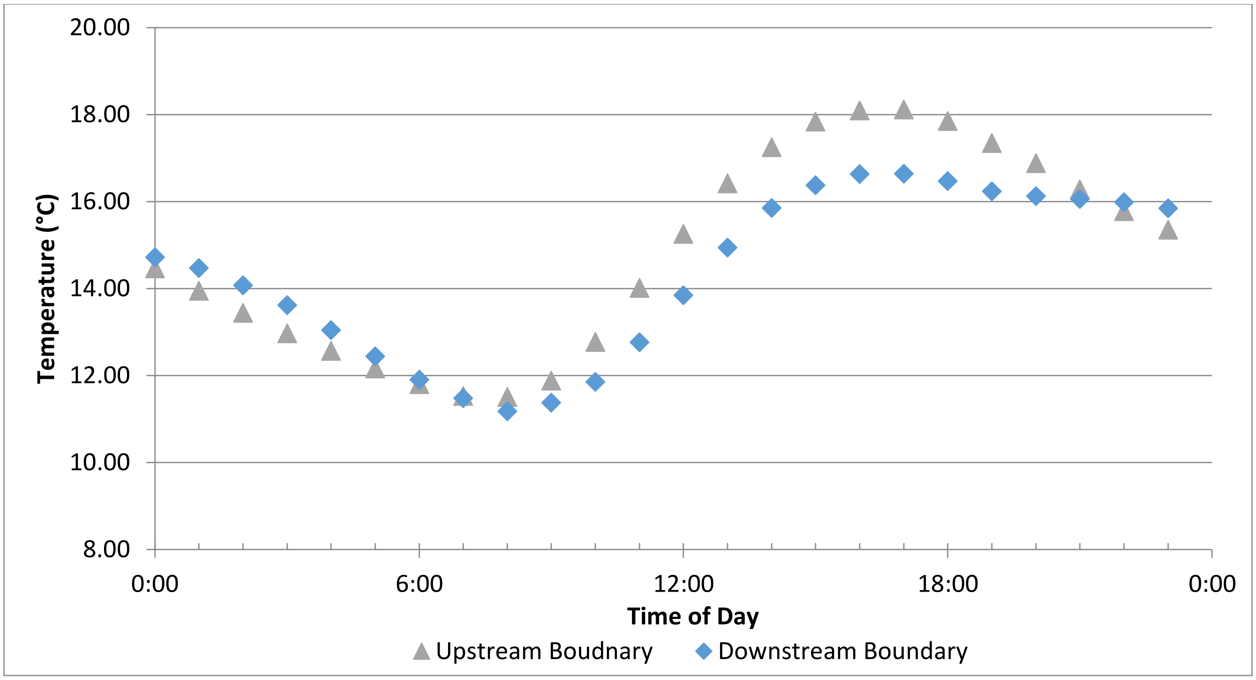

Figure 3: Diel Stream Temperature

3.1.2. Conductivity

Conductivity was continuously measured by sondes in the stream. Conductivity of a stream is generally related to the total dissolved solids. The model also accounts for mixing of other stream inputs, groundwater sources, or point sources assuming that the stream is completely mixed at the point of entry.

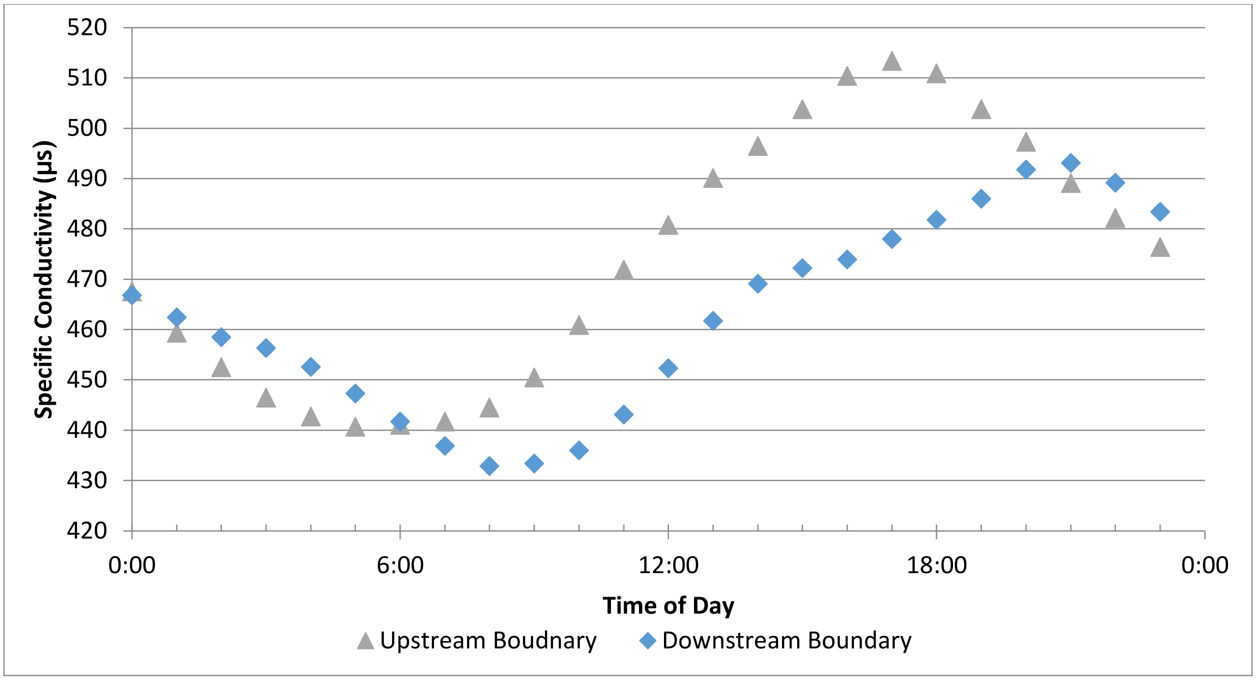

Figure 4: Diel Stream Conductivity

3.1.3. Inorganic Suspended Solids

Inorganic solids are a parameter of concern for some discharge permits and water quality. The model includes a settling rate that can be used to predict how inorganic solids settle in the reach. Grab samples were analyzed to determine inorganic solids concentrations.

Unfortunately there was an error in the first approximation of detritus and suspended solids. When repeating the experiment there was only enough sample left to run from the 9:00 am tests at each reach. All of these single points are used in the model as plotting points against the model predictions. The model inorganic solids are shown in Table IV.

Table IV: Inorganic Solids Concentrations

Location	Inorganic Solids Concentration (mg/L)
Whiskey Gulch (Upstream Boundary)	3.855
Beaver Dam	1.429
Rocker	0.909
I-15 Overpass (Downstream Boundary)	3.315

3.1.4. Dissolved Oxygen

Dissolved oxygen is a primary parameter of concern in this project. The dissolved oxygen concentrations were measured continuously by optical sensors on each sonde. This value was used to calibrate the model for the macrophytes in the stream. Everything that effects the dissolved oxygen balance was either measured or estimated in an attempt to leave macrophytes as the last unknown value in the model. The model was then adjusted so that the modeled dissolved oxygen concentration equaled the measured dissolved oxygen concentration. The difference between the outputs of the basic model, without macrophytes, and the adjusted model was assumed to be the effect on dissolved oxygen from macrophyte photosynthesis and respiration.

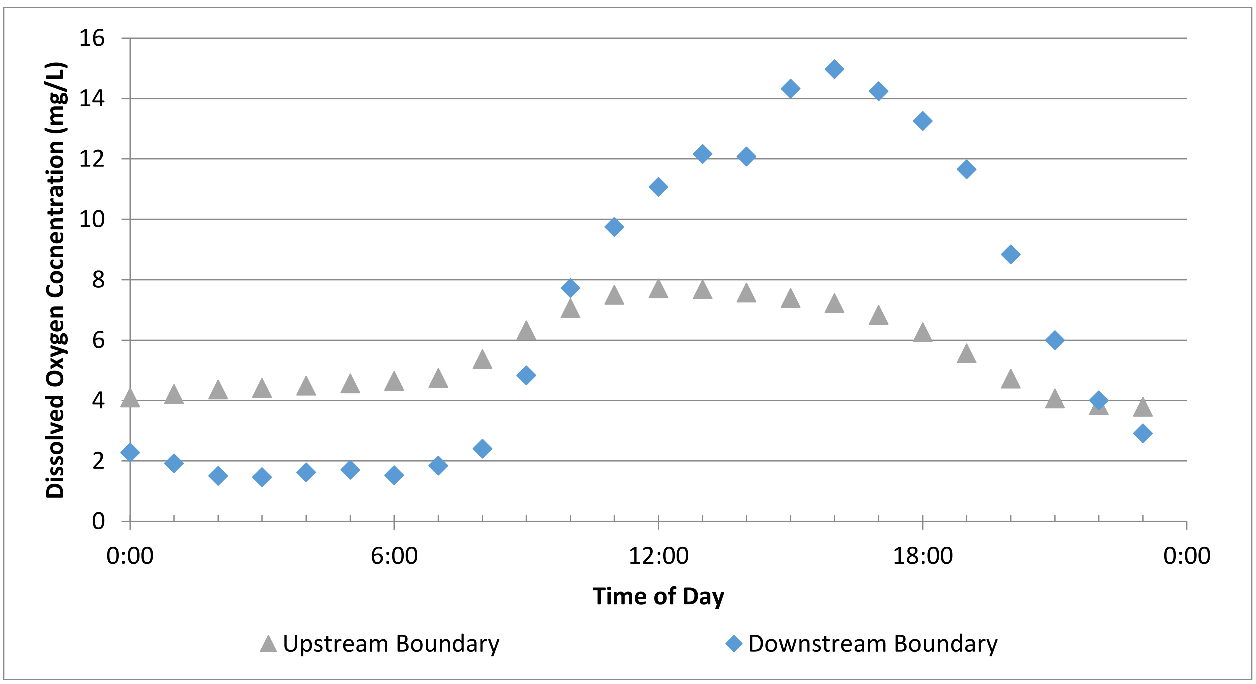

Figure 5: Model Dissolved Oxygen Concentration

3.1.5. CBOD

The model simulates two types of carbonaceous biochemical oxygen demand (CBOD); CBODslow and CBODfast. Each value can be given a different rate to account for systems where organics breakdown at different rates. However for the Silver Bow Creek, it was suitable to only use CBODslow to model the effects of the CBOD leaving the waste water treatment plant. The CBOD is one of the parameters that effect the dissolved oxygen balance of the stream the most. The WWTP measures BOD value for the day the model was run was converted to the ultimate CBOD value via the following equation (Flynn, Chapra, Pelletier, & Tao, 2015).

Equation (7): CBOD

$$C_t = C_U(1 - e^{-kt})$$

t = Time after C_U concentration (days)
C_t = BOD at time t (mg/L)
C_U = BOD ultimate (mg/L)
k = BOD consumption rate constant (day^{-1}) (5 day^{-1} was used in the model)

Small diel variation of CBOD loading is expected as the plant varies its output throughout the day. A series of CBOD tests were performed in the lab to estimate the CBOD values at each grab sample from the stream but the results from the experiment were unacceptable as they either did not consume at least 2 mg/L of oxygen or fell below 2 mg/L minimum.

3.1.6. Nutrients

Organic Nitrogen, NH_4-Nitrogen, NO_3-Nitrogen, Organic Phosphorus, and Inorganic Phosphorus were all determined using the FIA. Nutrient concentrations are affected by uptake or release by bottom algae, sediments, atmospheric transfer, and inputs and outputs from the stream section. The nitrogen concentrations affect the dissolved oxygen balance according to the nitrification and denitrification rates.

The large ammonia concentrations leaving the plant appear to undergo rapid nitrification to make up the majority of the nitrates present in the stream. The plant appears to discharge a fairly consistent amount of nitrate over the day. It is also important to note that there could be nutrient input from sources upstream, but these are small compared to the concentrations in the study reach. Table V compares the nitrate and phosphorus loading based on WWTP data and measured concentrations. While concentrations are close, there are discrepancies as expected since the upstream boundary is downstream of the WWTP outfall. Since the WWTP outfall is about 1.25 km upstream from the sample location, nutrient concentrations get modified by nitrification, denitrification, and uptake by macrophytes. The nitrate concentration is slightly higher and the ammonia lower due to denitrification. There is also a drop in total nitrogen which may party be a result of macrophyte uptake of nutrients.

Table V: Current Nutrient Loading

Location	Nitrate, NO_3 (lb/day)	Ammonium, NH_4 (lb/day)	Total Nitrogen (lb/day)	Phosphate, PO_4 (lb/day)
Upstream Boundary	108.44	381.43	489.87	64.477
WWTP	80.49	499.86	580.35	47.692

3.1.7. Detritus (Particulate Organic Matter)

The detritus value affects the heat and light portion of the model. More detritus in the stream will make it more turbid, and reduce the amount of light available for photosynthesis in the stream. These functions are for the benthic algae modeling, but since they affect the production of the macrophytes as well, they could be useful if the model can be modified to include a more comprehensive solution to macrophytes. There is also a settling rate and dissolution rate parameters available for the model to predict changing concentration and how it affects the CBOD of the stream.

The detritus only has a single data point for each reach. The values used for the model are listed in Table VI. It is important to note that the sum of detritus and inorganic suspended solids represents the total suspended solids (in the absence of phytoplankton).

Table VI: Detritus Values

Location	Detritus Concentration (mg/L)
Whiskey Gulch (Upstream Boundary)	3.374
Beaver Dam	2.088
Rocker	1.818
I-15 Overpass (Downstream Boundary)	2.431

3.1.8. Alkalinity

The alkalinity affects how easily the pH of the stream changes from other inputs. Alkalinity is affected by the photosynthesis of algae and macrophytes as they take in carbonate as a substitute for CO_2 when fixing carbon. This also leads to diel changes in alkalinity. Macrophytes take in more carbon during the day when photosynthesis is occurring, and releases more carbon at night when respiration is still occurring. While the model has methods to account for the algae, the impact of macrophytes is not modeled. Alkalinity is also affected by the temperature, concentration of CO_2 in the atmosphere (397.33 ppm), and the rates at which CO_2 dissolves in water (Earth System Research Laboratory, 2016). The bicarbonate buffer system will determine the equilibrium point for in stream alkalinity, but macrophyte interactions will affect its actual concentration (Lambers, Chapin, & Pons, 2008). Alkalinity values are measured using titrations performed on grab samples from the stream. The alkalinity value used for the upstream boundary was 133.70 mg $CaCO_3$/L, and for the downstream boundary was 115.85 mg $CaCO_3$/L.

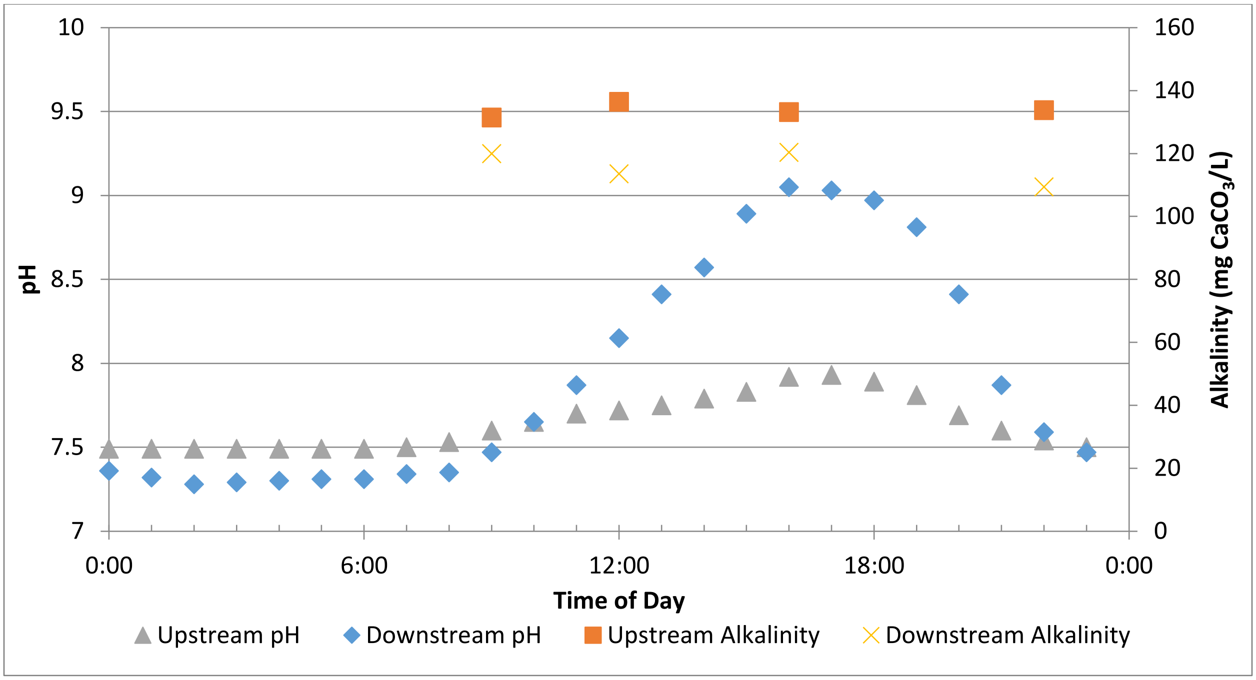

Figure 6: Diel pH and Alkalinity

3.1.9. pH

The pH of the stream and alkalinity are directly related to one another. pH of the stream is affected by many of the parameters including temperature, nitrification, denitrification, and macrophyte and algae respiration. Sondes were used to measure the stream pH.

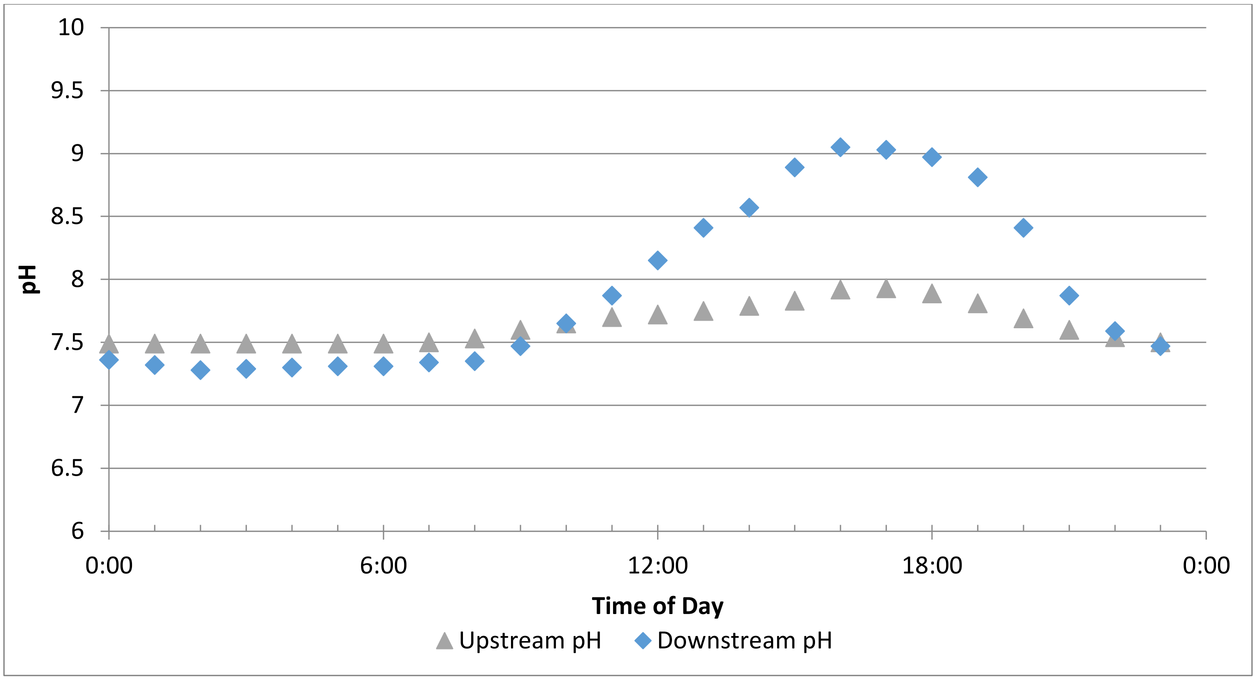

Figure 7: Model pH Input Values

3.2. Downstream

The downstream tab is composed of the same parameters as the Headwater tab, except there are no tributary options since the model requires everything to have mixed with the stream by this point. All of the data was measured at the same time as the headwater data using another set of sondes and grab samples. Downstream values are listed in the upstream graphs and tables.

3.3. Reach

The mainstream and any tributaries are divided into smaller subsections called reaches in the Reach tab. Each reach is designated with a number, and physical parameter data in input for each reach. The studied reach was divided into five reaches based on physical barriers and parameters. The first three reaches were defined by the beaver dams present on the stream. Since each dam was modeled as a broad crested weir each of these reaches can only contain a single element. The next reach follows the last beaver dam until stream enters a long channelized stretch, which marks the beginning of the last reach until the downstream boundary. These reaches were arbitrarily chosen to have 10 and 5 elements respectively.

3.3.1. Physical Parameters

Most columns, which are associated with individual parameters, are self-explanatory, such as reach length and downstream latitude and longitude. The location column asks you for the distance from the downstream boundary in kilometers. The element number determines how many individual sections the reach will be broken down into when performing calculations and plotting data. It is important to note that reaches with a weir can only have a single element. Elevation upstream and downstream, and downstream latitude and longitude columns are self-explanatory.

Reach elevations were determined by surveying the study reach. The depth of the main channel was measured wherever possible. The profile of the stream bed is shown below in Figure 8. The stream bed has a fairly uniform slope to it, with the dotted line representing a constant slope imposed on the actual stream bed profile.

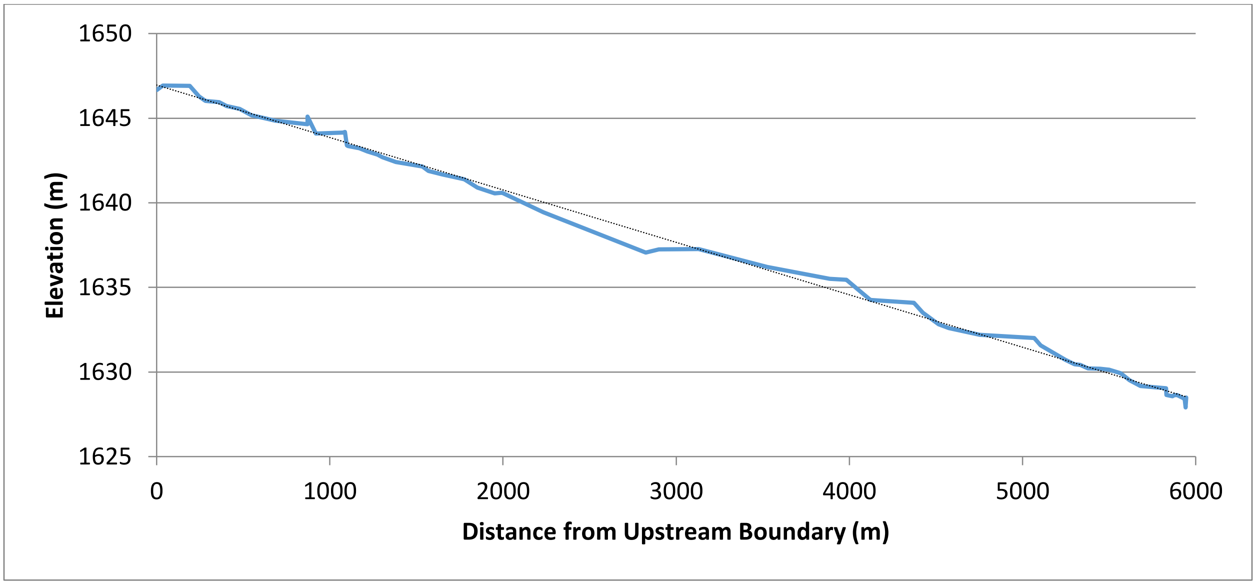

Figure 8: Stream Bed Elevation Profile

Silver Bow Creek was divided into five reaches based on the location of three beaver dams and where the stream becomes linear and channelized.

Table VII: Reach Parameters

Reach Number	Reach Length (kilometer)	Upstream Elevation (meter)	Downstream Elevation (meter)
1	0.191	1646.9	1646.7
2	0.680	1646.7	1645.1
3	0.205	1645.1	1644.1
4	4.258	1644.1	1630.4
5	0.497	1630.4	1628.6

3.3.2. Weirs

Several beaver dams along Silver Bow Creek were modeled as broad crested weirs. Height and width of the weirs were measured in field. The weir constant values, "adam" and "bdam" in the model, were retrieved from a paper that modeled beaver damns effects on water hydraulics (McCullough, Eisenhauer, Dosskey, & Admiraal, 2007). The effects of the beaver dams on water quality appear to be very small.

Table VIII: Beaver Dam Weir Coefficients and Dimensions

Reach	Weir Height (m)	Weir Width (m)	adam	bdam
1	0.20	7.00	1.69	1.5
2	0.20	7.95	1.69	1.5
3	0.30	11.20	1.69	1.5

Equation 8: Weir Equation

$$Q = adam * B * H^{bdam}$$

Q = flow (m^3/s)
$adam$ = constant
$bdam$ = constant
B = width of weir (m)
H = height of weir (m)

3.3.3. Rating Curves

Flow data from USGS gauge station 12323250 was used to calculate rating curves. The rating curves help the model to predict depth and velocity of water. This USGS station is located directly below the WWTP. ArcGIS software was used to estimate average widths of each reach when calculating the velocity rating curve for each independent reach. Flow is assumed to be constant throughout the reach, with no inflow or outflow from other sources or groundwater. Figure 9 below shows the rating curve plots with Table IX denoting the specific values of the empirical constants a and b for each reach. The depth α value is equal to 0.5335 and β is equal to 0.2607.

Equation (9): Rating Curve Velocity Equation

$$U = aQ^b$$

U = velocity (m/s)
Q = flow (m^3/s)
a = empirical constant
b = empirical constant

Equation (10): Rating Curve Depth Equation

$$D = \alpha Q^\beta$$

D = height (m)
Q = flow (m^3/s)
α = empirical constant
β = empirical constant

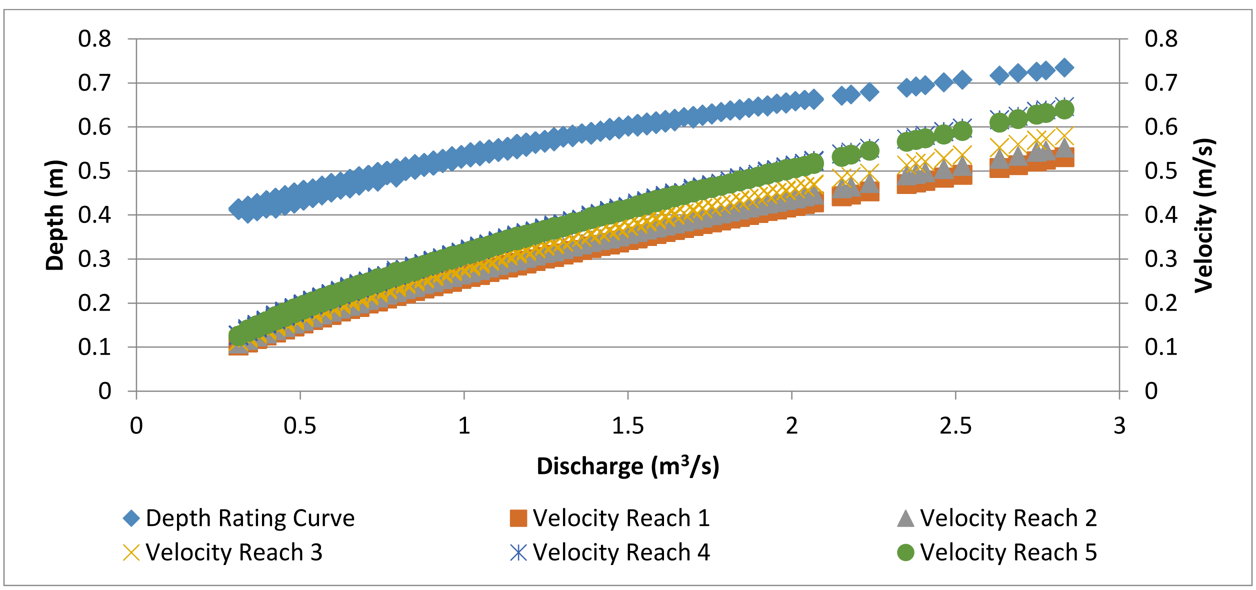

Figure 9: Rating Curves

Table IX: Rating Curve Values

Reach	Width (m)	a	b
1	7.256	0.2583	0.7393
2	6.970	0.2689	0.7393
3	6.647	0.2820	0.7393
4	5.965	0.3142	0.7393
5	6.031	0.3108	0.7393

3.3.4. Prescribed Values

This tab is contains a list of parameters that can be prescribed for individual reaches. The parameters included are dispersion, prescribed sediment oxygen demand, methane flux, ammonia flux, inorganic phosphorus flux, and evaporation.

The bottom algae coverage was set to 0% for all reaches. Even though the model has a built in feature for algae growth and impacts on the stream, they have very similar effects to macrophytes which would make distinguishing one from the other impossible. Benthic algae grows in the stream, but the impacts should be far less than those of the macrophytes which have a much larger biomass. The macrophyte approximations will contain the effects of benthic algae so it is really an estimation of the effects on water quality by photosynthetic organisms.

The very low dissolved oxygen concentrations prevented the sediment diagenesis model from working as intended, which caused a model error. In order to circumvent this, the sediment diagenesis model had to be turned off to allow the model to run to completion. After these modifications the model was no longer estimating the effect of the sediment oxygen demand so tests on the reach needed to be made to account for it in the model. Sediment samples were tested against water columns, which served as blanks to determine water oxygen demand, to estimate the sediment oxygen demand for use in the model. This laboratory-measured SOD was entered in the reach tab to account for its effects on the stream. The estimated SOD was 1.645 $g/m^2/d$. This value was estimated in the winter following the model sampling date. This value corresponds well with SODs observed in Oregon (1.3-4.1 $g/m^2/d$), but are likely underestimated since there is no macrophyte production or growth during the winter months. South Dakota has observed SOD values as high as 6.98 $g/m^2/d$ (Utley, Vellidis, Lowrance, & Smitth, 2008).

3.4. Reach Rates

The “Reach Rates” tab is for overriding the model calculated values for various rates, allowing for more accurate depictions of each reach. Since there are quite a few rates that can be prescribed, only the parameters used will be discussed. The following sections discuss how these values were estimated for the Silver Bow Creek.

3.4.1. Prescribed Reaeration

Initially the delta method was used to estimate a reaeration rate from sonde data in Silver Bow Creek, but the equations produced unreliable results because of the low dissolved oxygen content and variable flows from the waste water treatment plant (Chapra & McBride, 2005). Instead the reaeration rate was calculated applying the delta method to sonde data from Blacktail Creek, the headwaters of Silver Bow Creek. Where Blacktail Creek meets Silver Bow Creek is less than a mile away from the headwater site at Whiskey Gulch. Blacktail Creek contains most of the flow that makes up Silver Bow Creek, has similar sediments, depth, and velocity making it a suitable reach to predict the reaeration rate of Silver Bow Creek.

The delta method relates the time of peak dissolved oxygen in a diel cycle to the reaeration rate, shown in Equation 10 below (Srivastava). Sonde data was used to predict the reaeration constant every day for 19 days. There is some loss of accuracy since the sonde was set record dissolved oxygen concentrations every 15 minutes, which may lead to a slight skew in reaeration rate estimations. There were very few differences in reaeration, with most values between 11 and 12, and averaging to be 11.903 d^{-1} at about 14.5°C. This value was then corrected to 20°C using Equation 11, to a value of 13.561 d^{-1}.

Equation (11): Delta Method

$$k_a = 24 \frac{\left(\frac{12\pi}{f}\right)\cos\left(\frac{\pi\emptyset}{f}\right) - 1}{12\sin\left(\frac{\pi\emptyset}{f}\right) - \emptyset} \frac{1}{1 + \frac{0.83}{f}\sin\left(\frac{\pi\emptyset}{f}\right)}$$

k_a = reaeration coefficient (d^{-1})
f = photoperiod length (hours)
$\emptyset$ = lag time from solar noon to highest dissolved oxygen concentration (hours)

3.4.2. Nitrification Rate

Nitrification is the oxidation of ammonium to nitrate. The nitrification rate is a measure of how fast this process happens (Eby, 2004).

Equation (12): Nitrification

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+$$

A first order rate equation was used to estimate the nitrification rate. It is important to note that the rate constant estimated also accounts for the macrophyte and algae removal of ammonia from the stream. It is impossible to separate the effects of natural reactions, macrophytes, and algae on ammonia concentrations with the information currently available. Ideally the rate at which nitrification occurs and the rate macrophytes intake nutrients would be known. The nitrification of ammonia consumes dissolved oxygen in the stream, while the intake of ammonia by macrophytes does not. This results in a skew in nitrate and dissolved oxygen concentrations in model outputs since it is impossible to distinguish how much ammonia is consumed by each sink.

Equation (13): Generic First Order Equation

$$C = C_0(e^{-kt})$$

C = Concentration at time t
C_0 = Initial concentration
k = First order rate constant
t = Any time after C_0

Observed ammonia concentrations from August 22, 2015 were plotted versus travel time in the studied stream and a logarithmic curve was fit to the data available. The water temperature for this day was about 14.5°C, so the rate at 14.5°C was then converted to the rate at 20°C using Equation 6. The temperature corrected nitrification rate was 2.123 d^{-1}.

3.4.3. Denitrification Rate

Denitrification is the reduction of nitrate to another nitrogenous compound, generally nitrogen gas, but may also convert to nitrous oxide in very small amounts (Eby, 2004).

Equation (14): Denitrification to Nitrogen Gas

$$4NO_3^- + 5CH_2O_{(aq)} + 4H^+ \rightarrow 2N_2 + 7H_2O + 5CO_2$$

Equation (15): Denitrification to Nitrous Oxide

$$2NO_3^- + 2CH_2O_{(aq)} + 2H^+ \rightarrow N_2O + 3H_2O + 2CO_2$$

A first order rate was estimated for denitrification in the same manner as the nitrification rate. The nitrate concentration increased significantly between the first and second sample sites as the large concentrations of ammonia underwent nitrification. The first sample site was ignored again to achieve a more appropriate approximation. Such large concentrations of ammonia and macrophytes make predicting the actual denitrification rate impossible, and instead this value could be considered an “effective denitrification rate”. As the ammonia nitrifies it adds to the nitrates in solution. Macrophytes and algae are also consuming nitrates, removing them from stream. This all happens while it is being reduced to nitrogen gas or nitrous oxide, removing even more from solution. The calculated effective denitrification rate is impacted by all of these variables, skewing it in such a way that does not represent the actual rate, but accounts for the changes in concentration as well as possible with the current information.

Observed ammonia concentrations from August 22, 2015 were plotted versus travel time in the studied reach and a logarithmic curve was fit to the data available. The water temperature for this day was about 14.5°C, so the rate at 14.5°C was then converted to the rate at 20°C using Equation 6. The temperature corrected denitrification rate is 5.433 d^{-1}.

3.5. Meteorological Data

All meteorological data were downloaded from the local Bert Mooney Airport for the day of the model run. This is reasonable because of the airports relatively close proximity and elevation to the sampling slight. Meteorological data impacts the temperature model built into QUAL2K to estimate water temperature downstream which in turn impacts many of the rates. There are five tabs for meteorological data; air temperature, dew point temperature, wind speed, and cloud cover. Each parameter is set on its own tab and requires an hourly input for each reach allowing specific changes over a long reach. All of the reaches use data from the airport.

Table X: Meteorological Data

Time of Day	Air Temp (°C)	Dew Point Temp (°C)	Wind Speed (m/s)	Cloud Cover
12:00 AM	11.11	0.56	4.02	100%
1:00 AM	10.00	0.56	7.15	75%
2:00 AM	8.33	1.67	5.36	100%
3:00 AM	7.22	2.22	2.68	100%
4:00 AM	6.67	3.89	2.68	100%
5:00 AM	6.67	3.33	3.13	100%
6:00 AM	6.11	1.67	2.24	100%
7:00 AM	6.11	0.53	2.68	100%
8:00 AM	5.56	2.78	2.68	100%
9:00 AM	6.11	1.11	2.24	100%
10:00 AM	6.67	1.11	3.58	100%
11:00 AM	9.44	1.11	2.68	50%
12:00 PM	11.11	1.11	3.13	30%
1:00 PM	12.22	0.56	0.00	40%
2:00 PM	15.00	0.00	2.68	30%
3:00 PM	16.11	-0.56	2.24	10%
4:00 PM	17.78	-1.11	0.00	10%
5:00 PM	17.78	-1.67	0.00	10%
6:00 PM	16.67	0.56	2.68	10%
7:00 PM	15.56	0.00	3.58	10%
8:00 PM	13.89	-0.56	0.00	10%
9:00 PM	12.78	-0.56	3.13	10%
10:00 PM	11.11	-0.56	3.13	10%
11:00 PM	9.44	-0.56	2.68	10%

3.6. Shade

The shade tab in the model is for entering the fraction of potential solar radiation blocked by topography and vegetation. Shade values used in this model come from a separate model that estimates a diel cycle of shade on the reach. This model is used by the Washington Department of Ecology and is specifically designed for use with QUAL2K (Oregon Department of Environmental Quality, 1996). The model runs with Fortran 90 and uses Excel as a graphical interface, similar to how QUAL2K is run.

To run the model, known data such as elevation, stream parameters, and vegetation types nearby need to be entered on the Main Menu tab. For this model it was assumed that the vegetation was medium sparse along the length of the reach.

The model output will provide the fraction of potential solar radiation blocked by topography and vegetation in a table with hourly values than can be copied directly into QUAL2K. The model also provides a visual representation of the data, which is shown below.

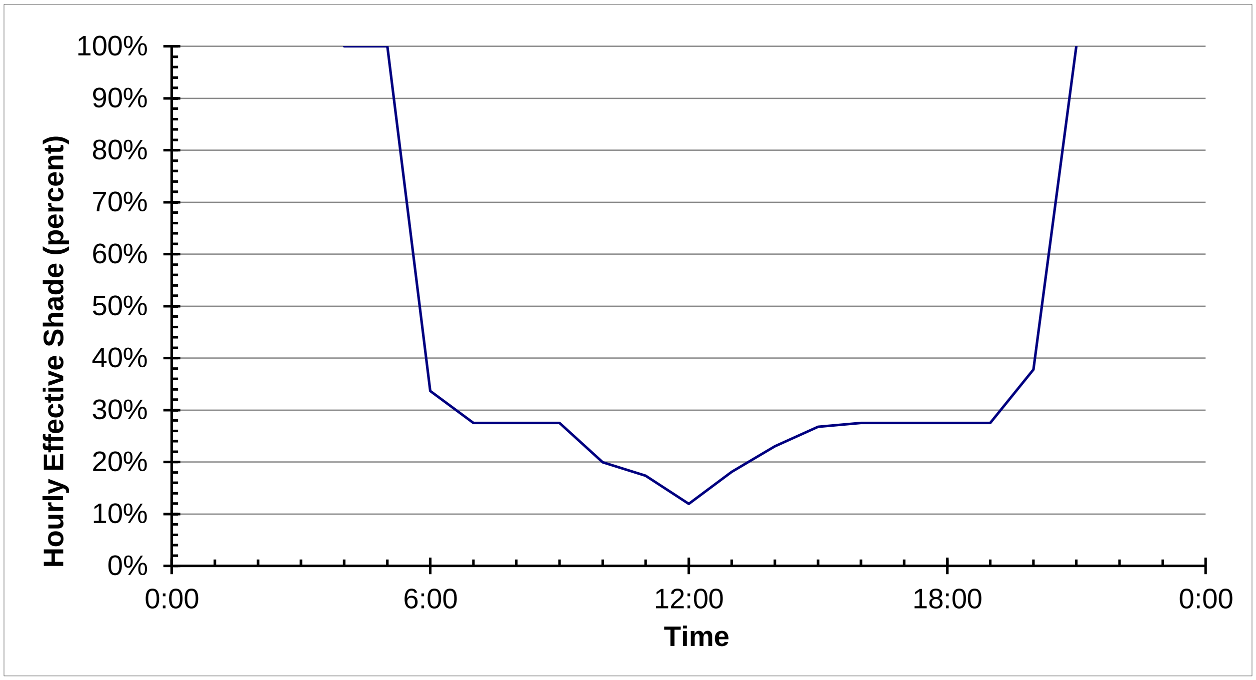

Figure 10: Shade Model Output

Table XI: Shade Model Values

Time of Day	Shade Coverage
12:00 AM	100%
1:00 AM	100%
2:00 AM	100%
3:00 AM	100%
4:00 AM	100%
5:00 AM	100%
6:00 AM	33.7%
7:00 AM	27.5%
8:00 AM	27.5%
9:00 AM	27.5%
10:00 AM	20.0%
11:00 AM	17.3%
12:00 PM	12.0%
1:00 PM	18.1%
2:00 PM	23.0%
3:00 PM	26.8%
4:00 PM	27.5%
5:00 PM	27.5%
6:00 PM	27.5%
7:00 PM	27.5%
8:00 PM	37.8%
9:00 PM	100%
10:00 PM	100%
11:00 PM	100%

3.7. Rates

The rates tab includes generic values for modeling reaches that can be modified to fit more specific needs. Very little modification was done to this tab since these values are generally used when modeling for total maximum daily loads. Each sub-heading contains cells for modifying specific rates or parameters.

3.7.1. Stoichiometry

This section defines the stoichiometry of organic matter to be used by the model. This applies to both detritus and phytoplankton masses. QUAL2K by default uses the Redfield ratio, an approximation defined by Dr. Chapra, one of the primary model developers (Redfield, Ketchum, & Richards, 1963) (Chapra S. , 1997).

3.7.2. Inorganic Suspended Solids

The only parameter that can be changed in this sub-heading is the settling velocity of suspended solids. The standard model value was used.

3.7.3. Oxygen

QUAL2K has several dissolved oxygen reaeration models built into it and this sub-heading has cells to select the model and the parameters that effect it. The reaeration rate was prescribed in the Reach Rates tab and therefore it was not necessary to change anything in this section.

3.7.4. BOD

BOD is again separated into "*Fast*" and "*Slow*" to account for different hydrolysis rates of different chemicals. If something is present in the water that breaks down and consumes oxygen very quickly then it is possible to give it a different loading and hydrolysis rate then say detritus which breaks down slower over time. For this project a single slow CBOD value was used.

3.7.5. Nutrients

Nutrients are divided into organic nitrogen, ammonium, nitrate, organic phosphorus, and inorganic phosphorus sub-headings. Each sub-heading contains cells of relevant information to change such as a nitrification rate for ammonium and a denitrification rate for nitrate. Altering these parameters would change the concentrations of nutrients that the model would predict. The nitrification and denitrification values were changed in the prescribed rate tab and were therefore not necessary to change anything here.

3.7.6. Detritus (POM)

The detritus sub-heading contains cells for dissolution rate, temperature correction, fraction of dissolution to fast CBOD, and setting velocity. This accounts for the particulate organic matter's impact on the oxygen demand in the stream. The values were not changed from the model default.

3.7.7. pH

The pH sub-heading only has a cell for the partial pressure of CO_2, which impacts the bicarbonate system in the stream. The only discoverable data was from Mauna Loa, and was estimated to be 397.33 ppm (NOAA ESRL, 2016).

3.8. Light and Heat

The Light and Heat tab contains all of the required rates and information for light intensity and surface heat transfer models. The photosynthesis-irradiance models are used for benthic algae calculations, but with model improvements could be used for an integrated macrophyte model as well. Surface heat transfer models are used to predict the temperature of the stream, which heavily impacts the rate of all water quality parameters. This section was not changed from the model default.

3.9. Macrophyte Compensation (Calibration)

The Point Sources tab was used to account for the macrophytes impact on dissolved oxygen concentrations in the stream. Ideally a diffuse source would be more accurate since it spread the demand evenly across the whole reach, but the diffuse sources tab does not allow for a time variable concentration of dissolved oxygen. Since diffuse sources can't be used, a series of point sources spread out evenly across the reach will approximate the same effect. Each point source adds a negligible amount of inflow to the stream so the flow of the stream is not increased. Next each point source is given a mean mg/L dissolved oxygen concentration, the range in which the concentration changes on a diel basis, and the time of maximum dissolved oxygen concentration. All of the point sources have large or negative concentrations to account for the dissolved oxygen mass balance needed and the fact that incremental change in flow is associated with these sources. The goal of adding the point sources is to change the total mass balance of oxygen without changing other parameters unaffected by macrophytes.

Each variable of the model was measured or estimated with the goal of only leaving the impacts of the macrophytes unknown. Since this is the last variable of the dissolved oxygen balance it was assumed that any disconnect between the values measured in the field and predicted by the model are a result of the macrophytes. After everything else was accounted for and finalized, the point sources were adjusted to make the model output as similar as possible to the observed data.

When correcting for macrophytes a single mean and range value was used for adjustments. Point sources were added every 0.05 km, with inflows of 0.00001 m^3/s. The mean mg/L value was -2000mg/L and the range was 12000 mg/L. The time of max concentration was 12:00 PM according to sonde data.

3.10. Observed Data

The final step to developing the QUAL2K model is entering data that is known or measured in the appropriate yellow tabs. These were all self-explanatory, entering hydraulics data into the Hydraulics Data tab or temperature data into the Temperature Data tab. The model will then use these values to plot points on the graphical outputs of the model predictions, allowing the user to compare observed data and model outputs. The impact macrophytes had on the stream were initially noticed because of the large disconnect between predicted data and observed data in stream.

4. Results and Discussion

All model outputs were generated using the data collected on August 22, 2015.

4.1. Reading QUAL2K Outputs

A sample QUAL2K model output is shown in Figure 13. Lines on the graph represent data that the model predicts along the reach. Points, or the square boxes in this case, represent the data from field measurements. The black points and line are the daily average values of the parameter on August 22, 2015, where the red points and lines are the daily maximum and minimum values of the parameter. The y-axis is always the unit each parameter is measured in, temperature in this case. The x-axis is always the distance from the downstream boundary, or endpoint of the model. QUAL2K outputs are always displayed from upstream to downstream, with the downstream boundary, or zero point, on the right side of the graph. The starting boundary is the furthest point away from the downstream boundary, and therefore is the largest value and farthest to the left on the x-axis.

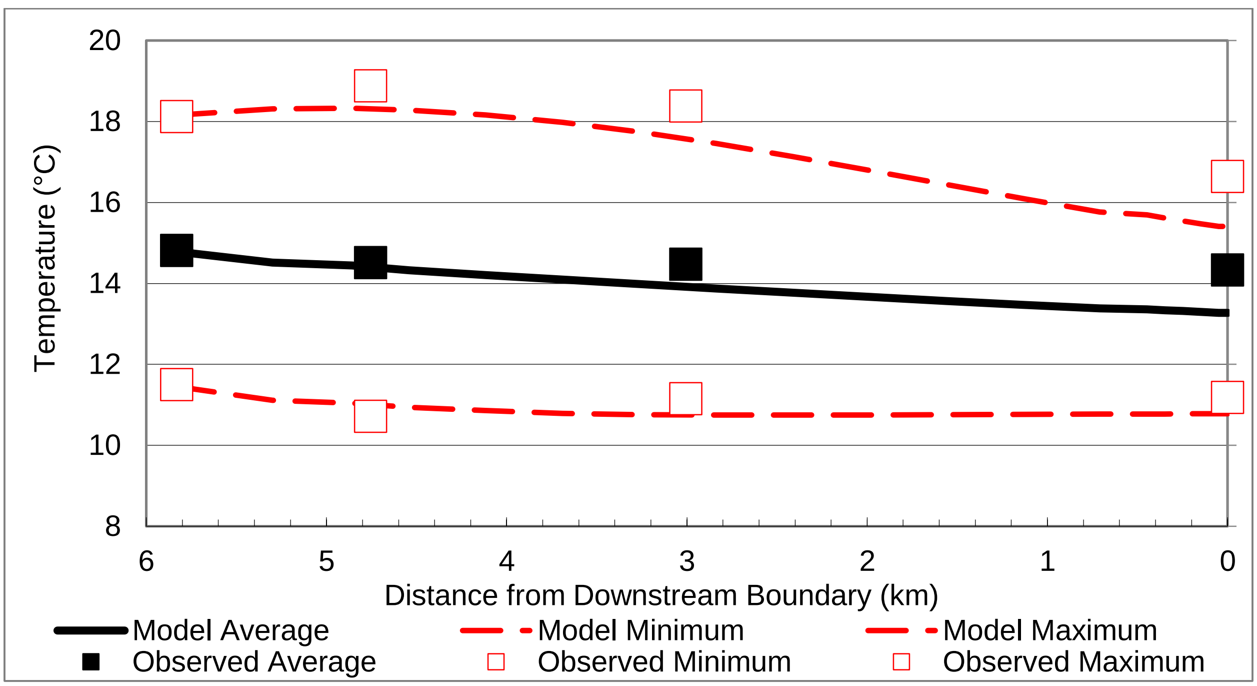

Figure 11: Model Temperature Output

4.2. Flow

The presence of macrophytes prevented the measurement of stream flow to compare to the model, but the model output shows that the point sources should not significantly impact the flow modeling. This is still assuming that there is no inflow or outflow of groundwater or other sources.

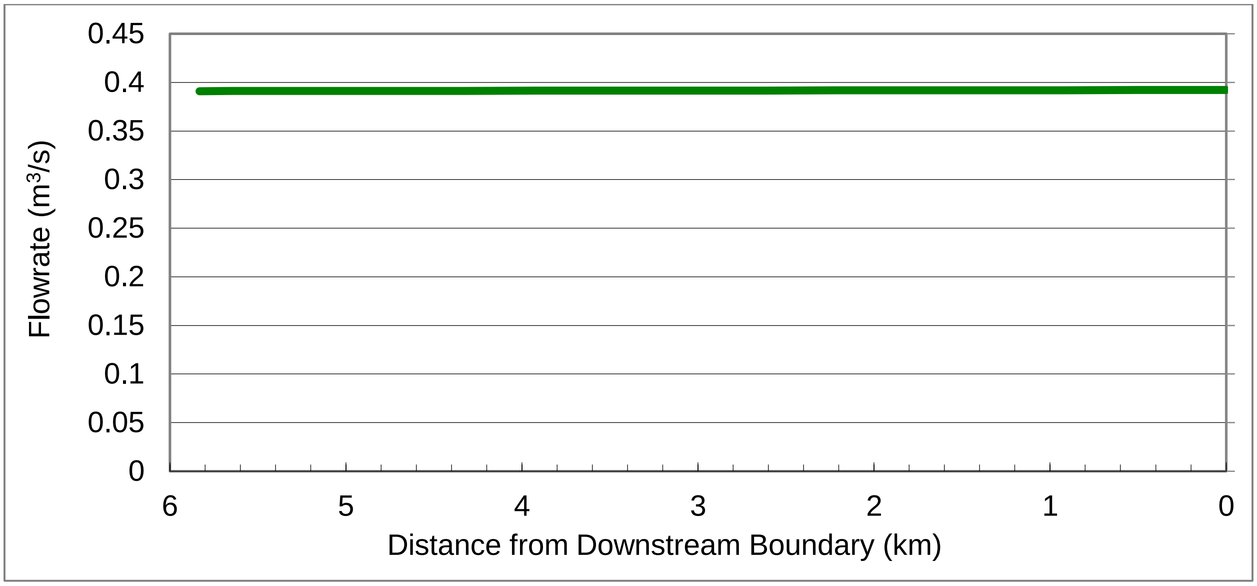

Figure 12: QUAL2K Flow Output

4.3. Velocity

There is no field data with which to compare to model outputs since the macrophytes made measuring the velocity of the reaches impossible.

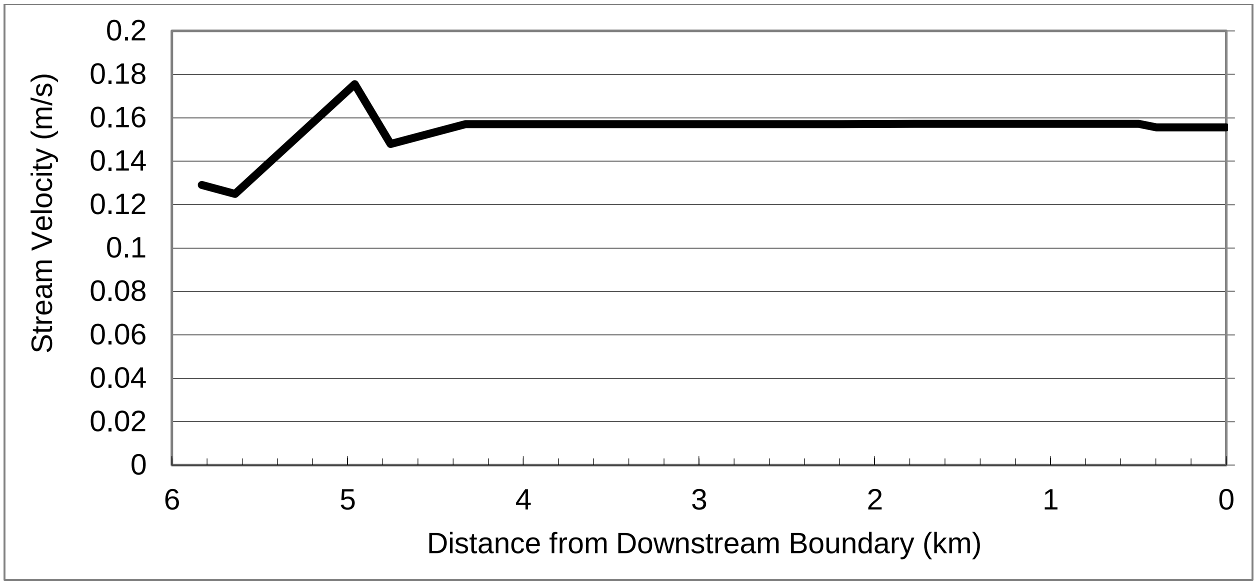

Figure 13: QUAL2K Velocity Output

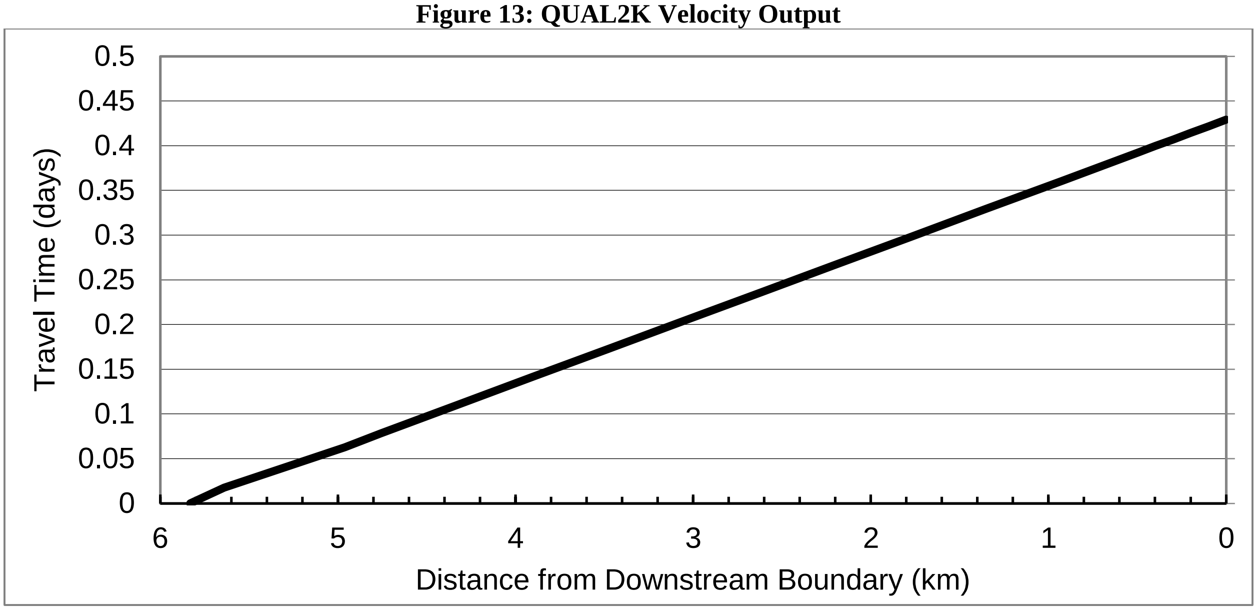

Figure 14: QUAL2K Travel Time Output

4.4. Depth

The depths of the stream will slightly vary for each reach because of the slightly different rating curves for each reach. This appears to be a good approximation for the average depth.

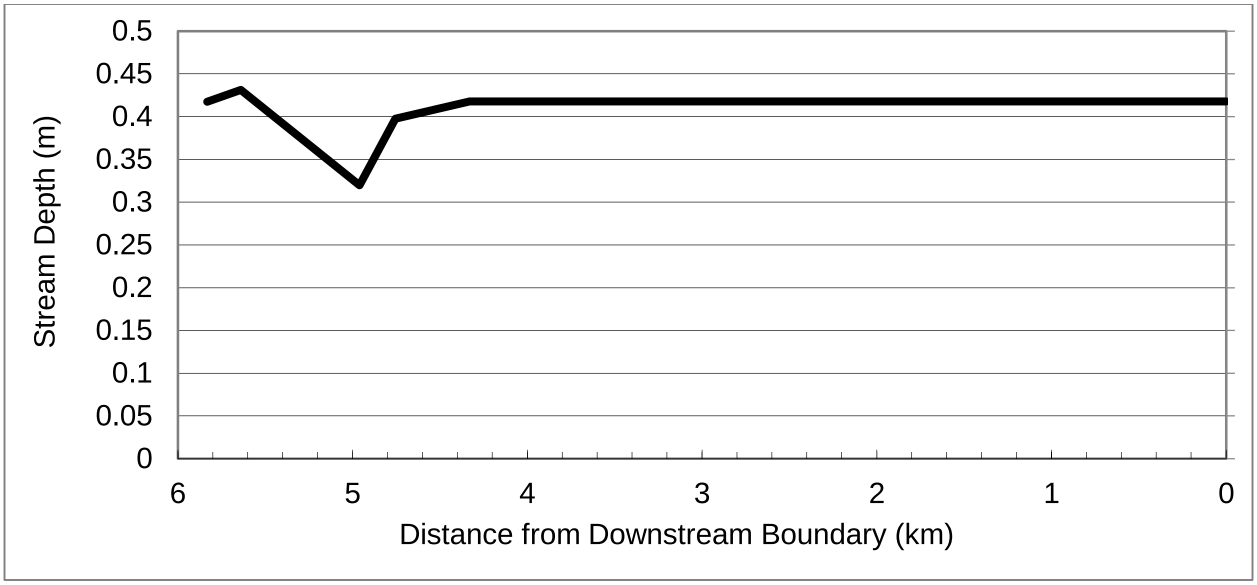

Figure 15: QUAL2K Depth Output

4.5. Dissolved Oxygen

The dissolved oxygen output without incorporating point sources to represent macrophyte effects on dissolved oxygen does not predict the extreme swing of concentrations that are observed. The prediction to the daily averages are reasonable, but does not fully represent the maximum and minimum concentrations observed in the stream. Macrophytes are capable of both supplying and consuming significant amounts of dissolved oxygen over the course of a single day.

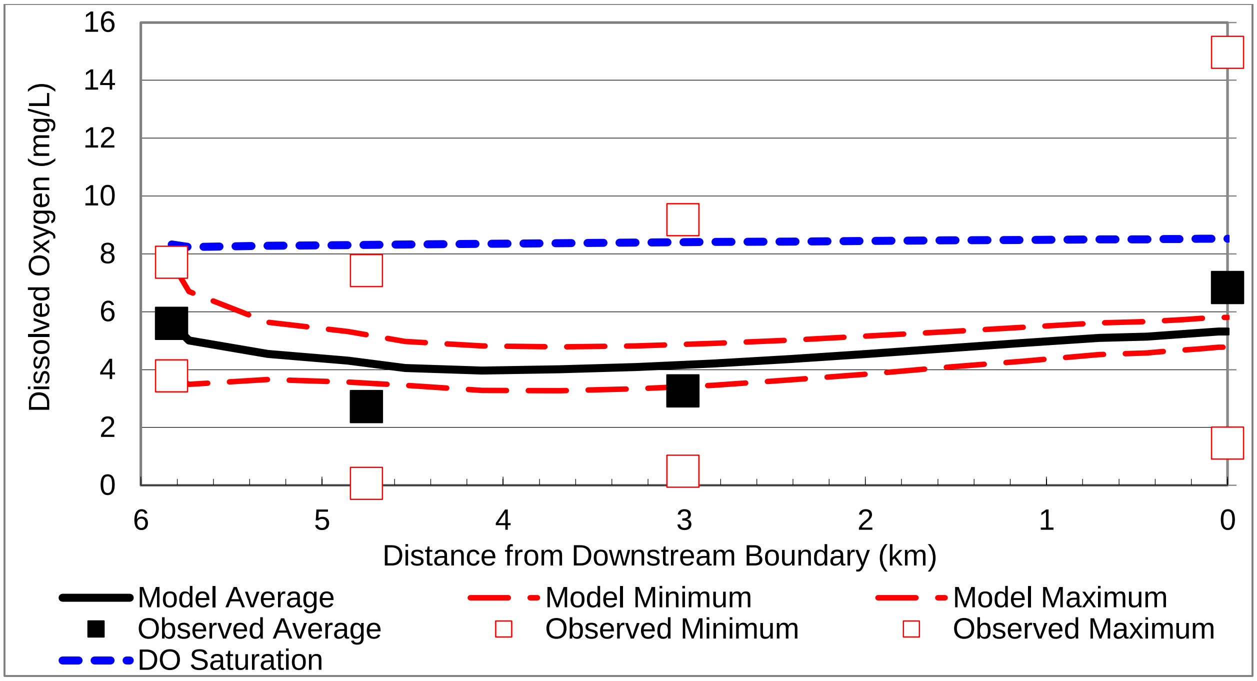

Figure 16: QUAL2K Dissolved Oxygen Output without the Effects from Macrophytes

After adjusting for macrophytes by adding point sources to the model the predicted minimum and maximum values are much closer to the observed values. The model predicts a smaller dissolved oxygen than was observed at the end of the reach. This is mostly likely caused by the model only assuming 12 hours of daylight and photosynthesis rather than the actual 14 hours of daylight on August 22, 2015.

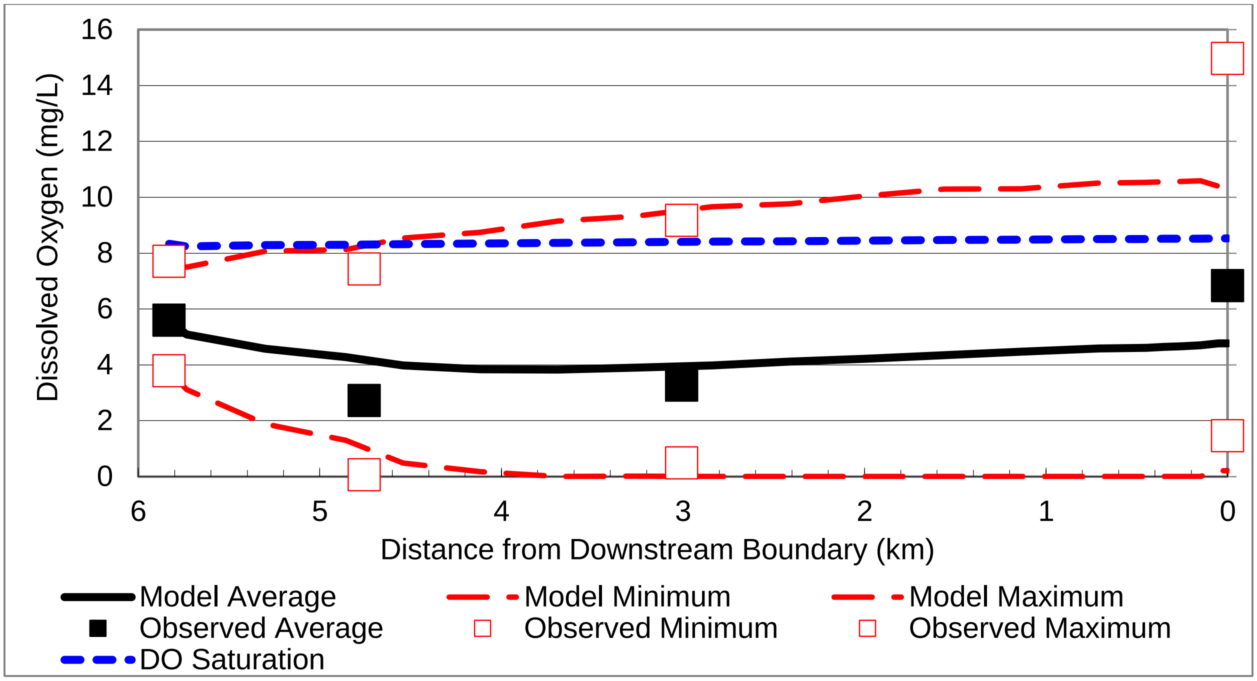

Figure 17: QUAL2K Dissolved Oxygen Output with Effects from Macrophytes

On August 22, 2015, the length of daylight was about 14 hours. The model approximates the point sources with a sine curve, a mean, and a range. Since it uses a generic sine curve it assumes half of the time, 12 hours in a day, it is above the mean, and the other half it is below the mean. This model assumption does not provide the best approximation for August 22, since macrophytes were photosynthesizing for 14 hours that day.

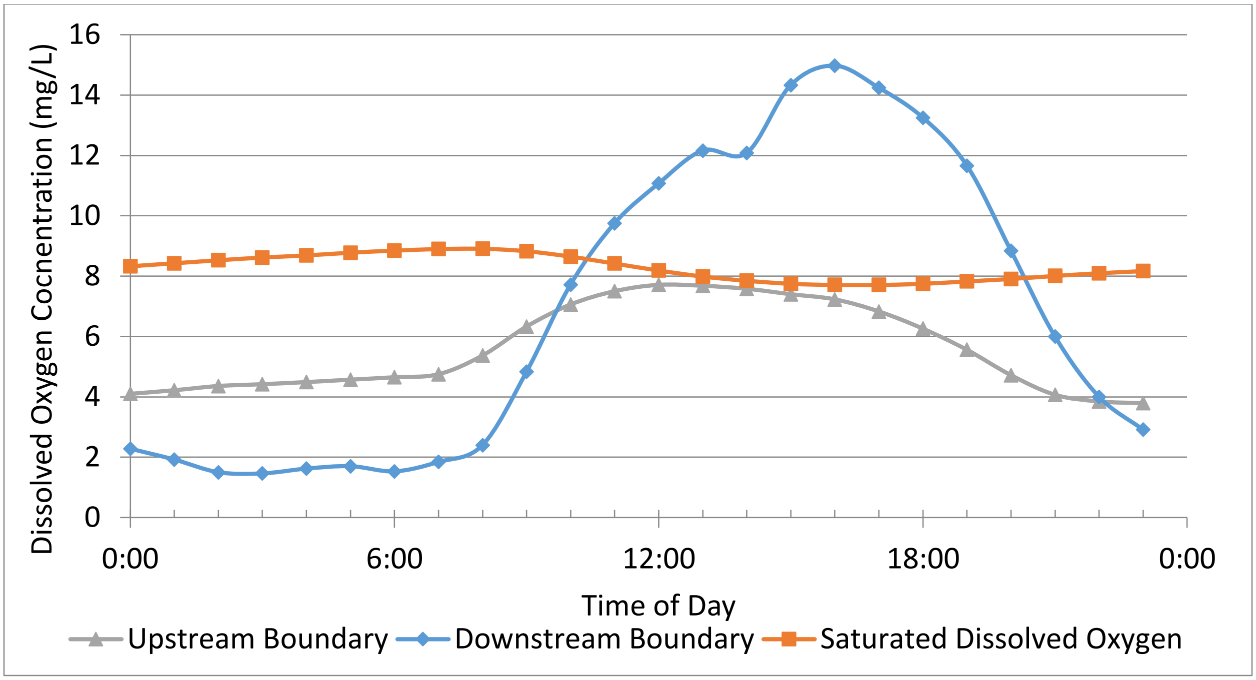

Figure 18: Dissolved Oxygen vs Time of Day

Figure 18 demonstrates the large diel impacts of macrophytes on Silver Bow Creek. The upstream boundary is exposed to less macrophytes and shows less diel changes then the downstream boundary. The concentration of macrophytes present in stream is large enough to super saturate the water with dissolved oxygen, causing it to actually emit oxygen to the atmosphere for about 10 hours on the modeled day.

4.6. Temperature

The temperature predictions from the model match up very well with the measured temperatures of the stream. The slight differences could be a result of incorrect cloud cover or shade approximations on the reach. Any error in the heat budget could change the temperature model. Since the model is off by a degree Celsius or so this will lead to a slight error in rate constant estimation, but should not greatly affect dissolved oxygen prediction.

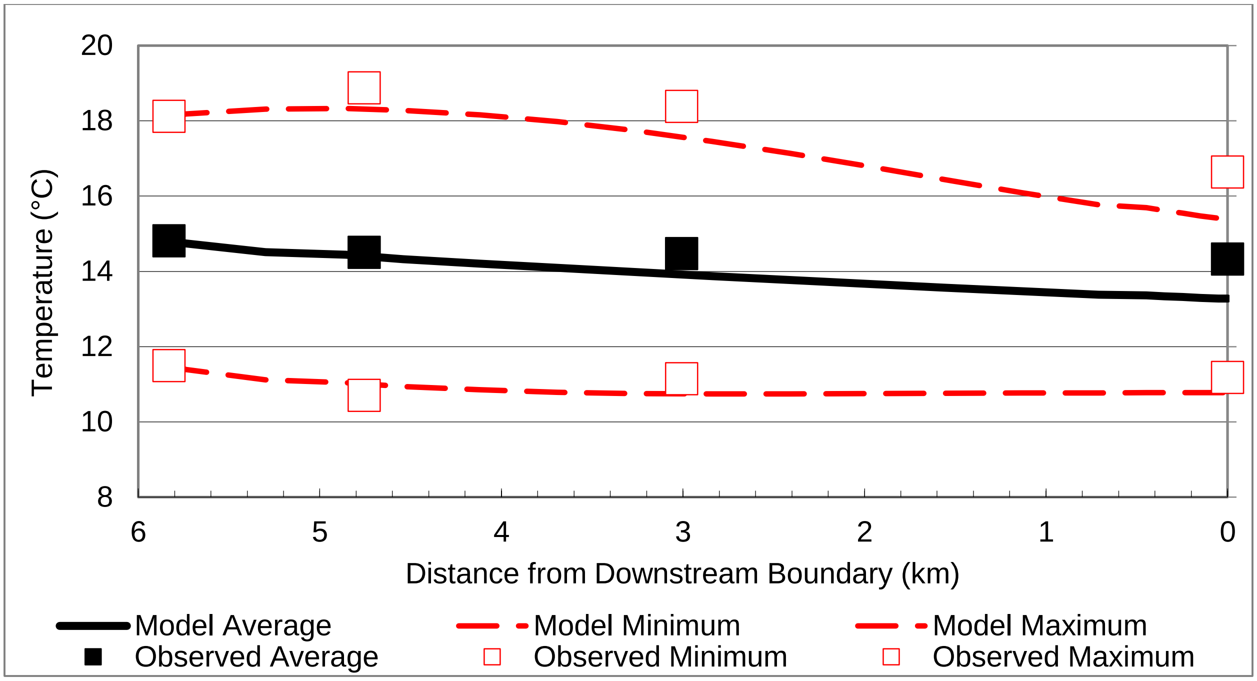

Figure 19: QUAL2K Temperature Output

4.7. Conductivity

QUAL2K predicts a very small decrease of conductivity over time. There is a discrepancy between the conductivity at the Rocker sonde and the model predictions, but overall seems to be an excellent approximation.

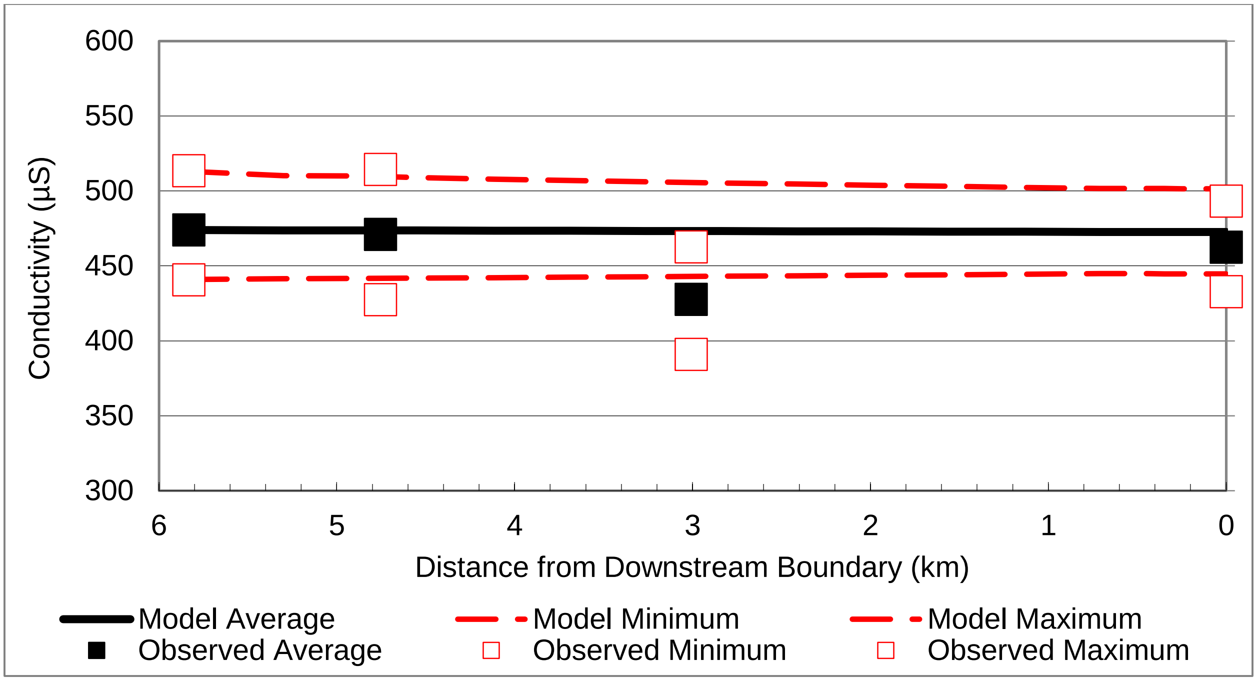

Figure 20: QUAL2K Conductivity Output

4.8. Inorganic Suspended Solids

There is a fairly large difference between the QUAL2K model output and sampled data for inorganic suspended solids. This is most likely due to the several beaver damns located between the first and second sampling points which act as sedimentation basins. Since the velocity is slower and the residence time is longer in these areas, more particulate settles out than the model predicts will.

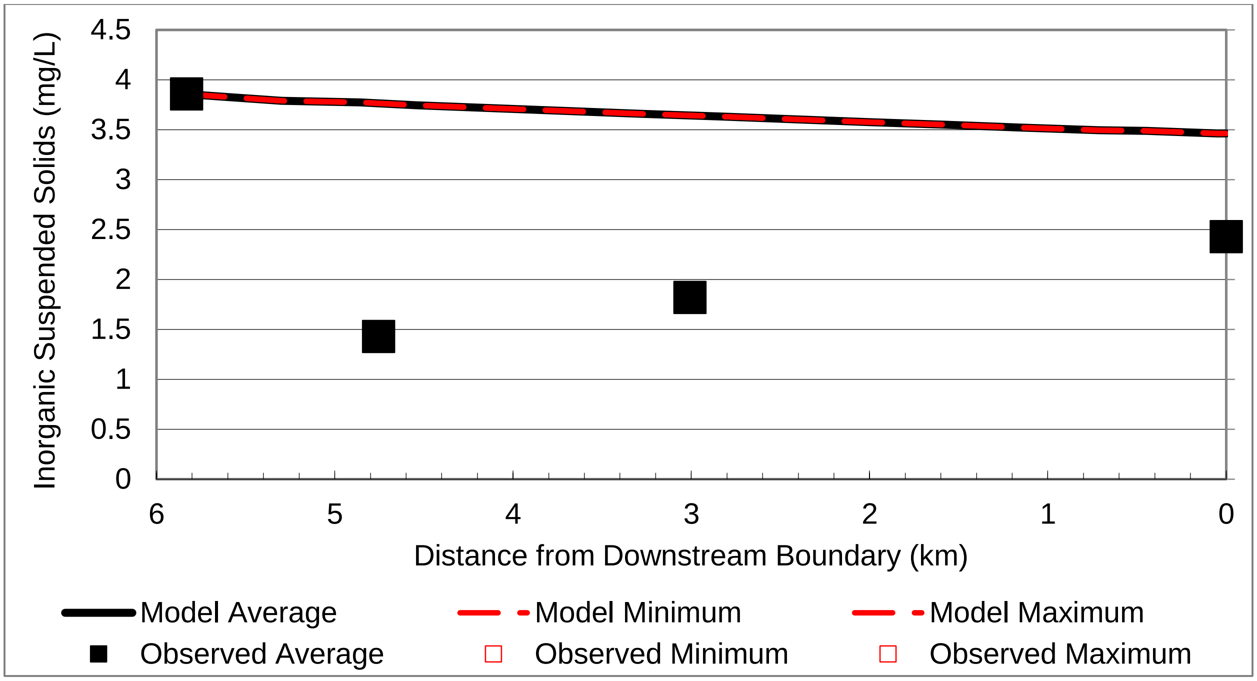

Figure 21: QUAL2K Inorganic Suspended Solids Output

4.9. Detritus

The amount of detritus the model predicts is reasonably close to the measured levels. It is important to note that floating or dead macrophytes will contribute to detritus in the stream, which is likely the reason why the last point is higher than predicted. Overall the settling rate and dissolution rates appear to be sufficient for estimation.

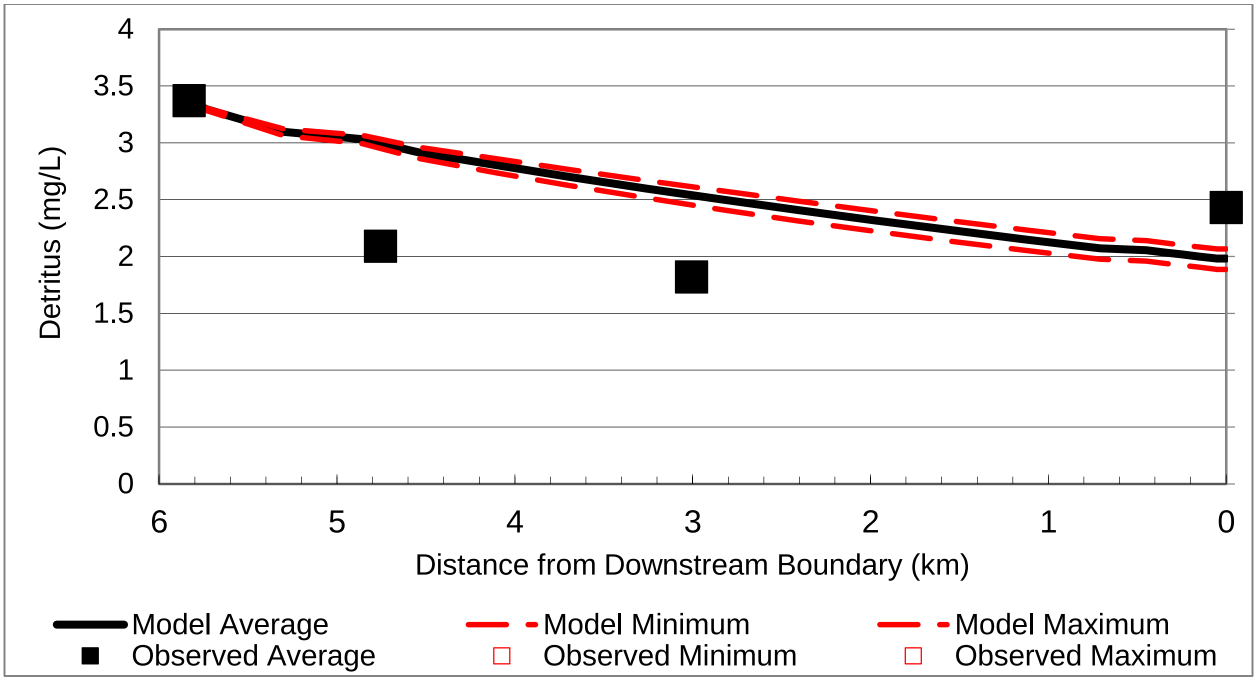

Figure 22: QUAL2K Detritus Output

4.10. CBOD

The CBOD curve looks exactly as expected, decreasing exponentially over time to near zero by the end of the reach. It is impossible to say for certain if this is a good estimation for CBOD concentration or the CBOD consumption rate without observed data to confirm the model.

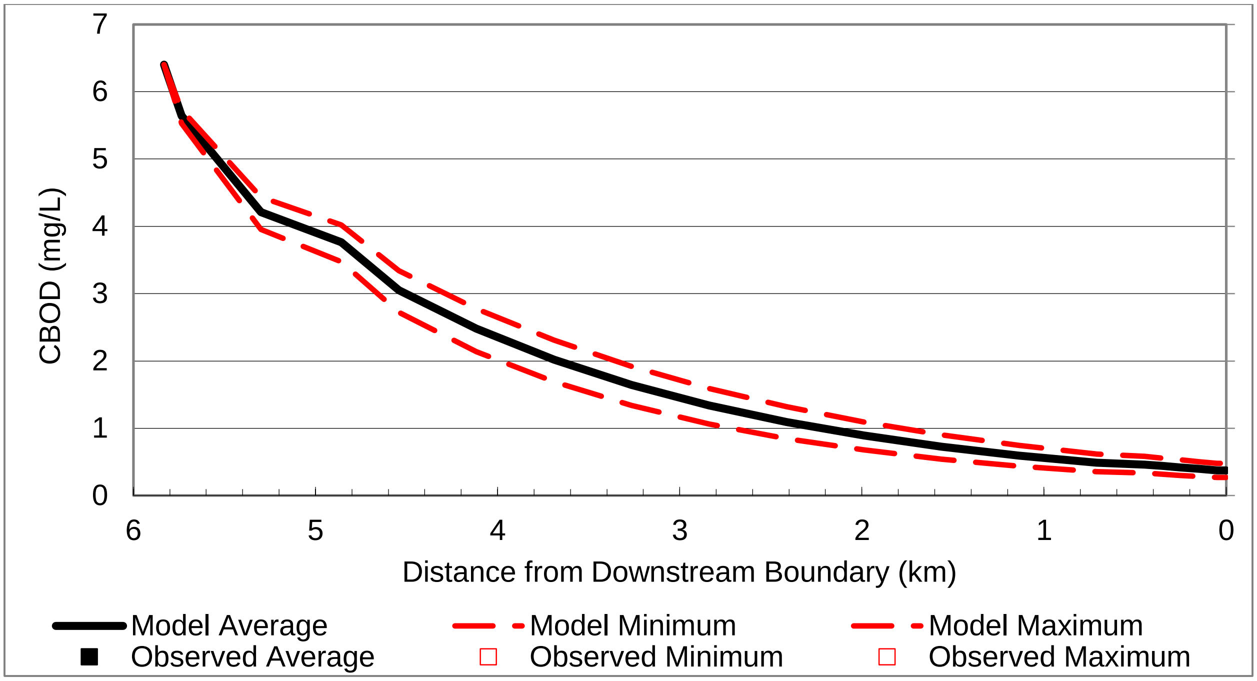

Figure 23: QUAL2K CBOD Output

4.11. Nitrogen

It appears that the WWTP discharges a fairly constant amount of nitrates, with highly variable ammonia loading. As the ammonia undergoes nitrification it is converted to nitrate, which explains the sudden increase in nitrate concentration seen downstream of the WWTP as the decreasing concentration of ammonia roughly correlates with the increasing concentration of nitrates.

The model output predicts far less reduction in organic nitrogen than actual measured values. This is most likely because the model does not account for macrophyte uptake of nitrates and ammonia. Macrophytes and algae both use inorganic nitrogen as a macronutrient, requiring it in large quantities to grow. This figure also infers that the macrophytes are using the water column as a significant source of nutrients. Organic nitrogen is total Kjeldahl nitrogen minus ammonia.

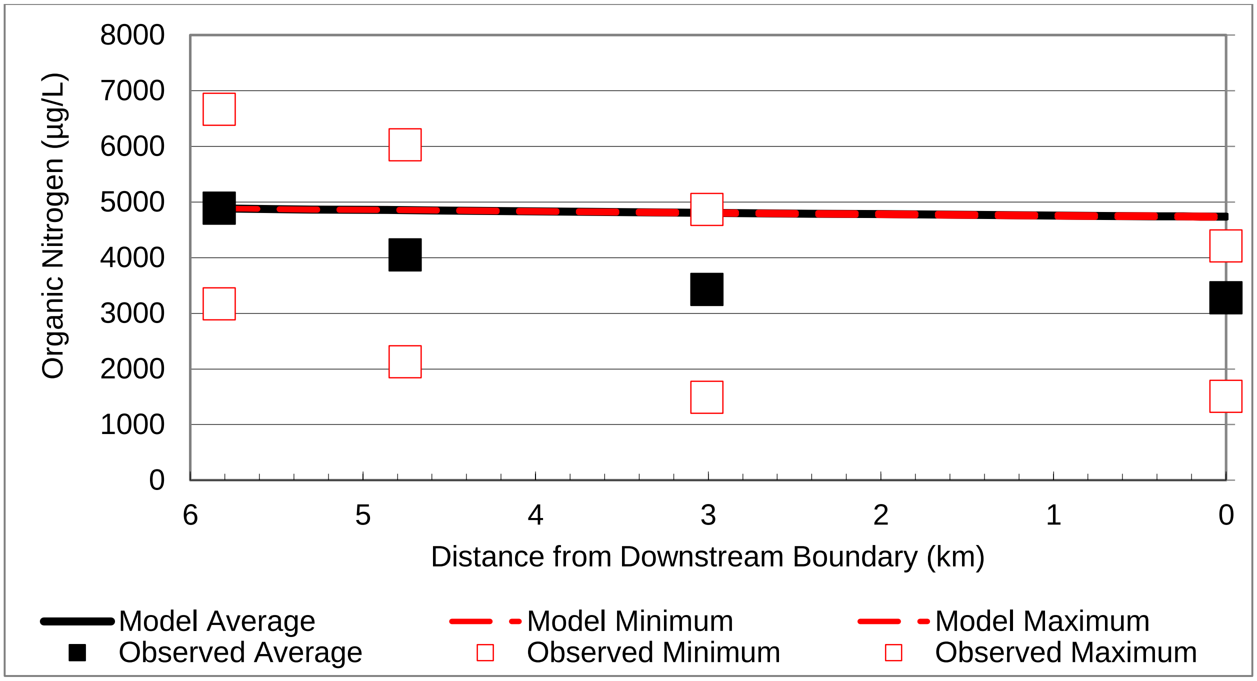

Figure 24: QUAL2K Organic Nitrogen Output

By using the average values of nutrients in the headwater the model does not fully characterize the diel change of nutrients. The average concentration from the upstream boundary is likely a result of sampling at times that weren't necessarily representative of the average. 24-hour sampling for nutrients would more accurately predict nutrient concentrations in stream.

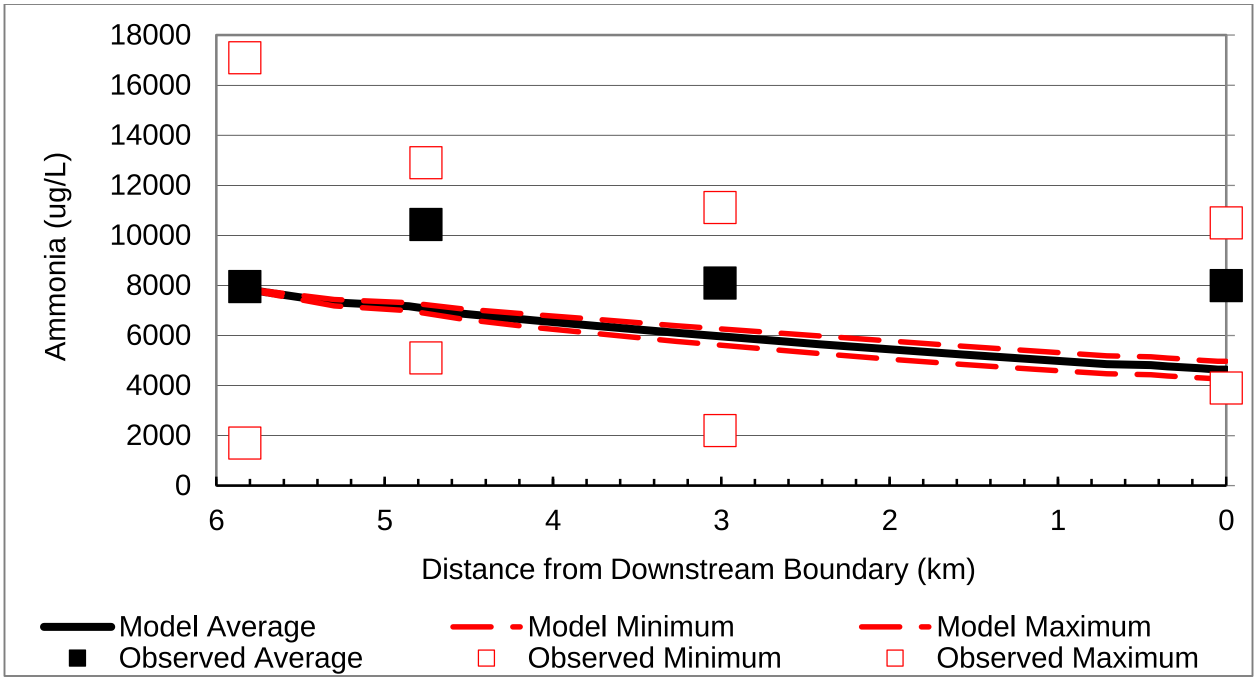

Figure 25: QUAL2K NH_4 Output

The nitrate output shows the significance of macrophyte uptake of nutrients versus the nitrification of ammonia. QUAL2K predicts a much higher concentration of nitrate than is observed because of the incorrect first order denitrification rate. The calculated nitrification rate accounts for all of the ammonia that leaves the stream and incorrectly assumes it all undergoes nitrification since the model does not account for ammonia taken in by macrophytes. The ammonia that leaves the stream by macrophyte absorption has no oxygen demand associated with it, and does not undergo nitrification. In future work it will be important to separate the effects of nitrification and macrophyte uptake when building the model.

It appears that the model is not working as expected for nitrate concentrations. There should be an initial increase in nitrate as the large concentrations of ammonia undergo the nitrification process and become nitrate. The nitrate should then be taken in by macrophytes and undergo denitrification to nitrogen gas. It appears that the net increase of nitrate from nitrification is greater than the denitrification and macrophyte absorption for a portion of the reach between the Whisky Gulch and beaver dam sample sites. After beaver dam the denitrification process and macrophytes should remove more nitrate from the stream than is added by nitrification of ammonia. Low dissolved oxygen concentrations will inhibit the denitrification process. The model is assuming all of the nitrate is leaving via denitrification, but in reality some if it is also being absorbed by macrophytes. The large disconnect in observed and predicted values is because the model is predicting a small rate of denitrification because of the low dissolved oxygen and not accounting for the macrophyte uptake.

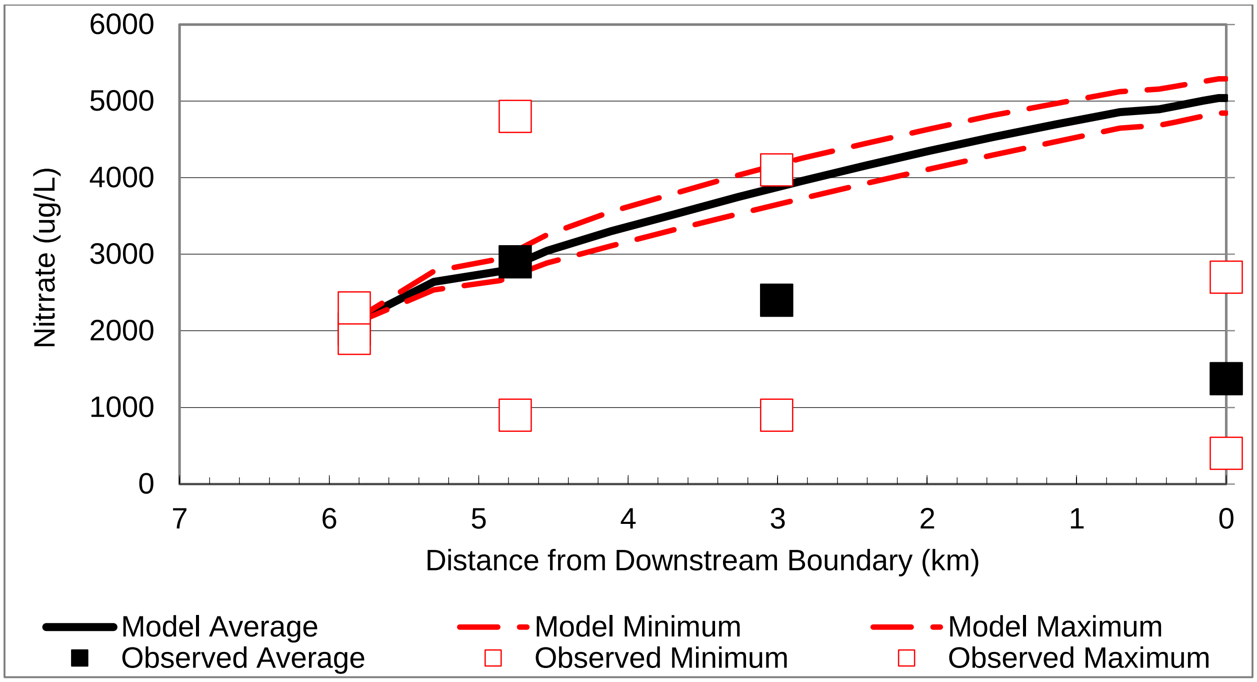

Figure 26: QUAL2K Nitrate Output

4.11.1. Phosphorus

The model predicts a fairly constant amount of phosphate in the stream, which matches the first and last average points well. The sample from the Rocker location is an outlier, but since the stream was only sampled 4 times in a day at each location there is a possibility that the times when the stream had the predicted concentrations was missed. Macrophytes and algae both require phosphorus to grow so the slight decreasing trend in observed data could be because of their uptake.

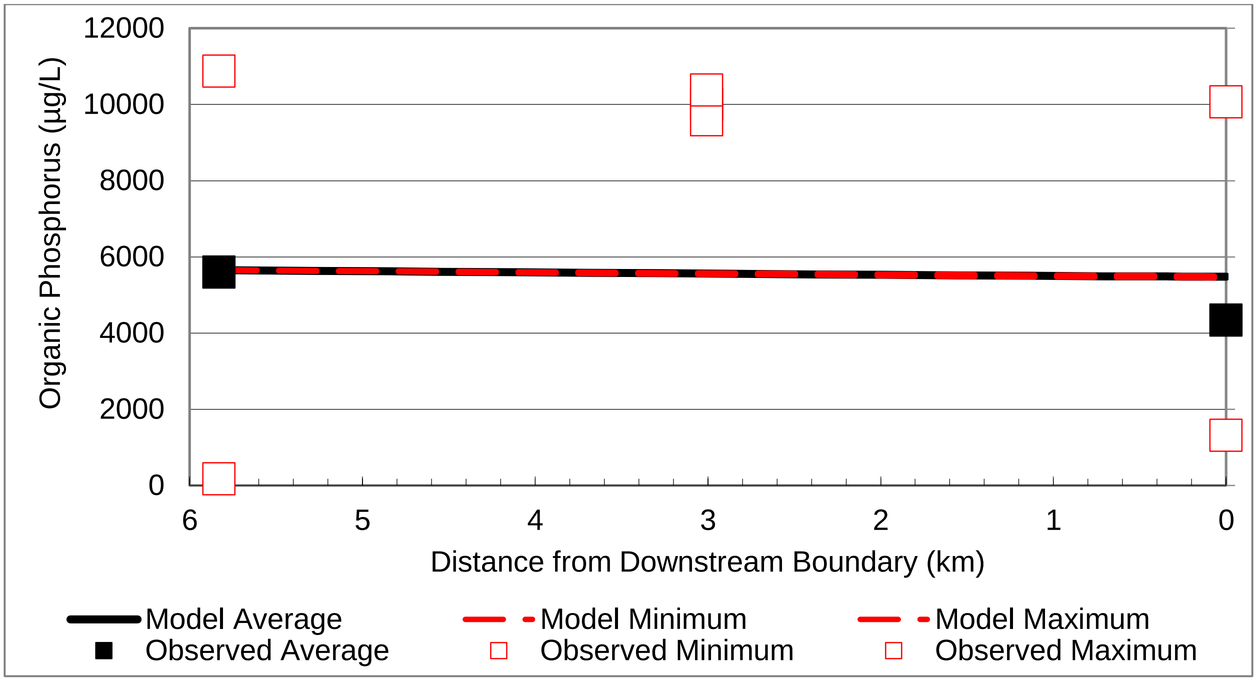

Figure 27: QUAL2K Organic Phosphorus Output

The model interprets the slight decrease in organic phosphorus as contributing to inorganic phosphorus. It appears that macrophytes and algae prefer to take in inorganic phosphorus, since it is in a more usable state unbound from organic molecules. As a reminder, macrophyte and algae intake of nutrients is not currently being modeled. Their contribution to the nutrient balance in stream is likely what causes the deviation between observed and predicted data.

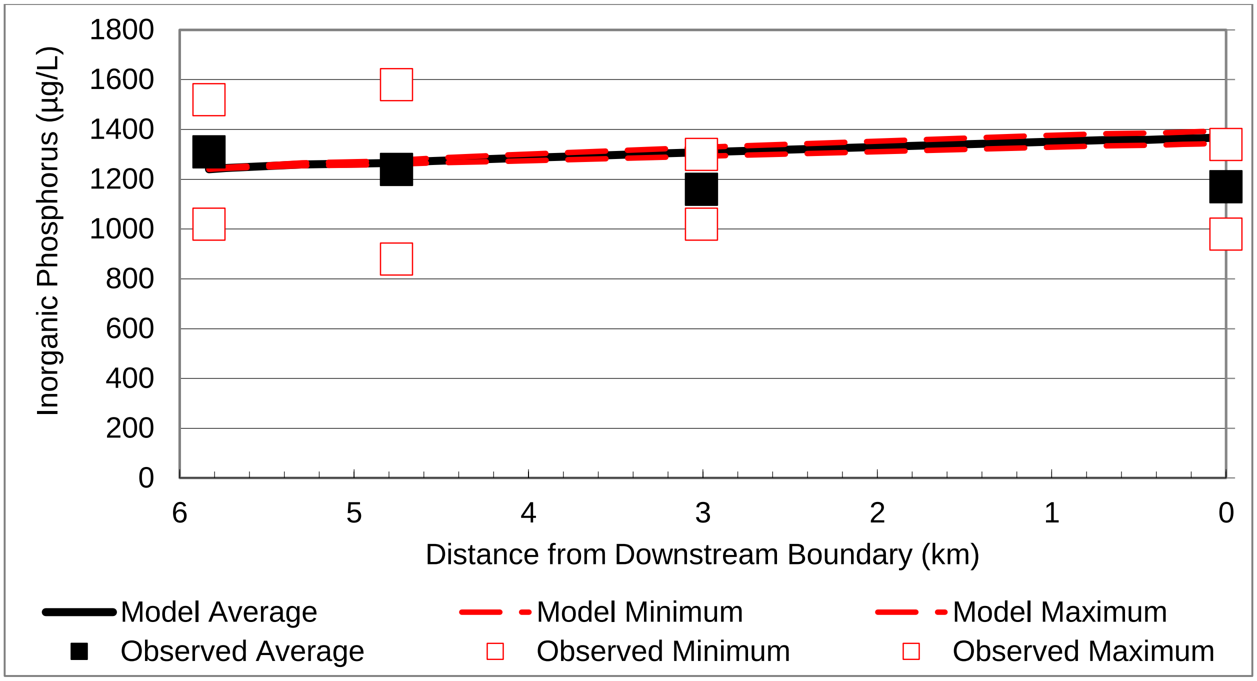

Figure 28: QUAL2K Inorganic Phosphorus Output

4.11.2. Alkalinity

The QUAL2K model output follows the observed alkalinity trends very well. The slightly lower observed alkalinity could be a result of macrophytes fixing bicarbonate during peak photosynthesis whereas the model is not simulating this process.

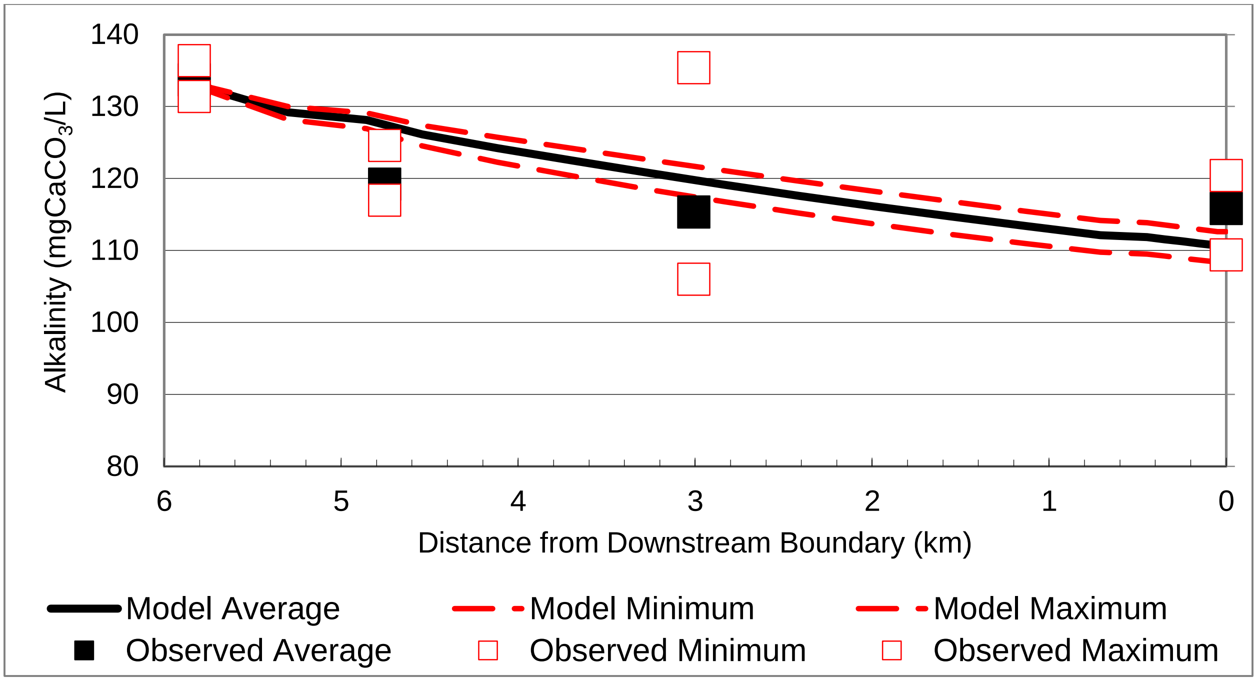

Figure 29: QUAL2K Alkalinity Output

4.11.3. pH

The model output for pH follows measured values very closely, except for periods where the photosynthetic activity is the greatest. At the Rocker location the effects of peak photosynthesis are especially noticeable, as the pH is greater than 9 for part of the day.

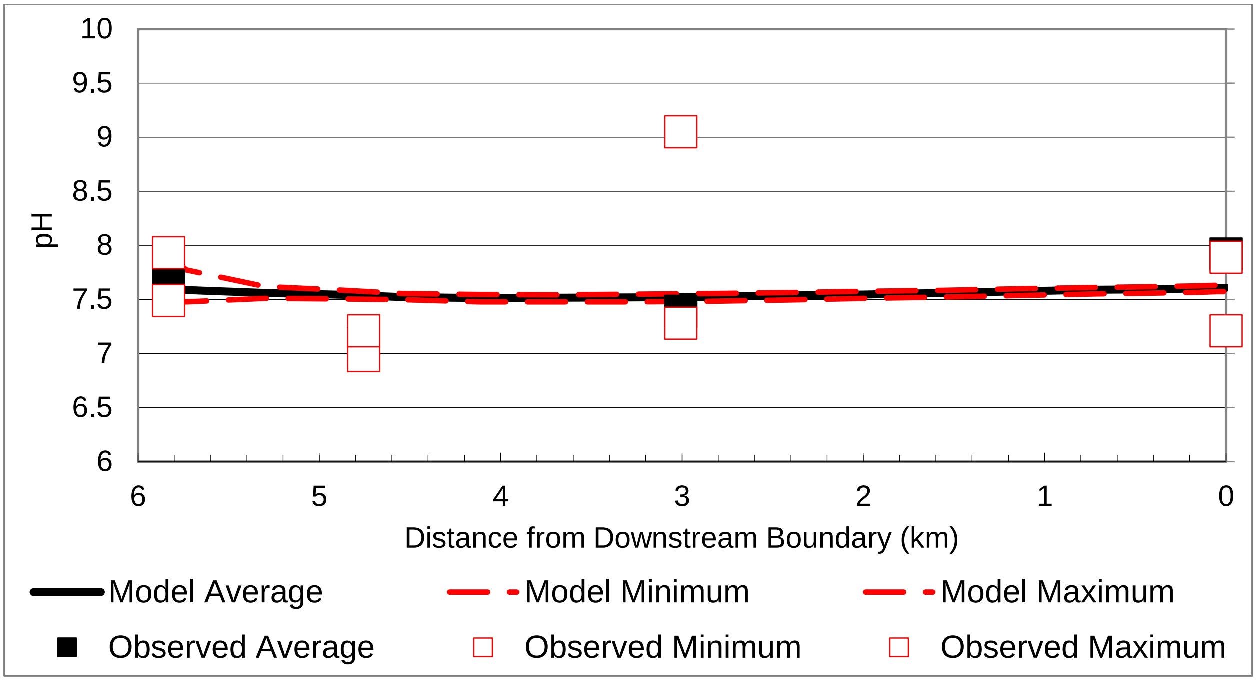

Figure 30: QUAL2K pH Output

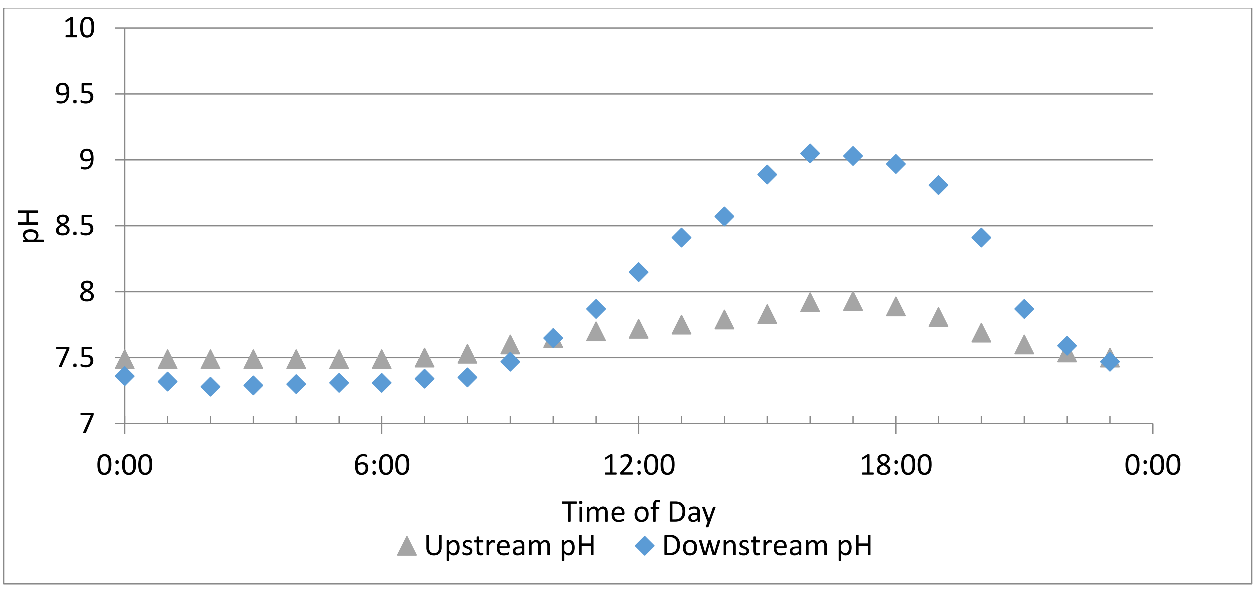

Figure 31: Diel pH

As expected, the downstream boundary of the model shows a more pronounced diel change in pH because of photosynthesis fixing large amounts of carbon dioxide and bicarbonate faster than can be replenished from the atmosphere.

4.12. Total Maximum Daily Load (TMDL) Analysis

The QUAL2K model was run iteratively to determine loads and associated concentrations of nutrients that would not impair the dissolved oxygen for Silver Bow Creek. Two methods were used when approaching this, one that assumes the macrophyte density in the stream will remain constant regardless of nutrient changes, and one that assumes macrophyte density decreases linearly with nutrient loading. Realistically the actual value should be somewhere between these, which will provide a best case and worst case scenarios. The percent reduction required to meet desired water quality were found by trial and error runs of the model.

Silver Bow Creek is designated as a Class I stream, which means the goal for dissolved oxygen concentrations are 5.0 mg/L for early life stages and 3.0 mg/L for other life stages. Silver Bow Creek is headwaters to the Clark Fork River, which is listed as a B-1 classification (Montana Department of Environmental Quality, 2016). For a class B-1 stream, the one day minimum instantaneous dissolved oxygen concentration required for early life stages of fish is 8.0 mg/L if the early life stages are in gravel spaces, and 5.0 mg/L if they are exposed directly to the water column, and 4.0 mg/L for other life stages (Montana Department of Environmental Quality, 2012). With the dissolved oxygen concentrations entering the reach below 8 mg/L a portion of this reach will always be impaired. The lowest concentration of dissolved oxygen entering the upstream boundary at Whiskey Gulch is below 4 mg/L, meaning even the 5 mg/L standard is impossible to reach without improving upstream conditions or increasing the dissolved oxygen of the WWTP outfall. Older life stages can survive with oxygen concentrations as low as 4.0 mg/L, which should be attainable.

The minimum goal of preventing hypoxic conditions has also been estimated for the studied reach. Hypoxia happens when dissolved oxygen falls below the concentration necessary to sustain most animal life, which is generally below 2.0 mg/L (USGS, 2016) (Boesch, 2008).

The 4.0 mg/L dissolved oxygen protects the health of fish and more mobile species. These mobile species are capable of moving away from areas of low dissolved oxygen to more oxygen rich environments. The 2.0 mg/L dissolved oxygen concentrations will protect species that are less mobile and not capable of leaving the areas of the stream that are hypoxic. If achieving a 4.0 mg/L of dissolved oxygen is too expensive or not feasible, then the stream should at least be above hypoxic conditions to protect aquatic life other than fish.

Since the model starts 1.25 km below the WWTP, any improvements to the effluent will improve the water quality before it reaches the modeled reach. These improvements are not capable of being modeled with the information currently available. This also means the model will provide a more conservative estimate of the reductions necessary to achieve the water quality goals.

4.12.1. Constant Macrophyte Loading

The constant macrophyte density model assumes that the macrophytes are capable of maintaining their current density regardless of concentrations in the water column. While they are able to exploit the nutrients available in the soils, it is unlikely that they will be able to grow to their current density without the existing nutrient concentrations in the water column. This method will provide a worst case scenario estimation for dissolved oxygen concentrations since macrophytes are largely responsible for the large diel variation and the resulting instantaneous dissolved oxygen concentrations falling below critical levels.

Assuming the macrophyte biomass stays constant, even if there was 100% percent removal of nutrients from Silver Bow Creek, there would still be hypoxic conditions. The effect of this macrophyte density is simply too large to prevent the large diel changes in dissolved oxygen and hypoxic conditions during night time. The current model uses a sine curve approximation for dissolved oxygen, assuming 12 hours of sunlight and 12 hours of night time. Realistically there was only about 10 hours of night time during the day the model was ran, which over compensates the night cycle in the model. This results in the model removing more oxygen then it should. While this provides for a conservative estimate it might not reflect realistic approximations of dissolved oxygen.

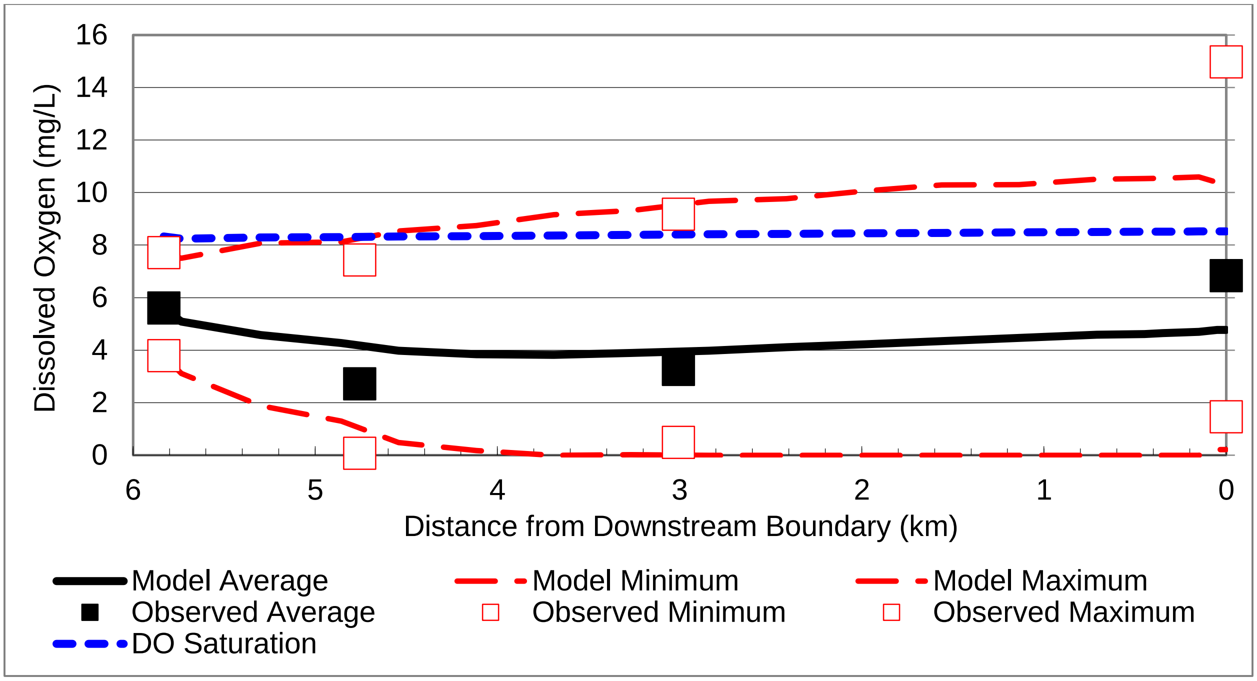

Figure 32: Dissolved oxygen concentrations modeled with the same macrophyte density as was determined in the calibrated model

Since a decrease in available nutrients will decrease the amount of macrophytes that can be supported, a method that accounts for that should provide a more accurate approximation.

4.12.2. Decreasing macrophyte Biomass and Associated Oxygen Production/Consumption

Reducing macrophyte loading with a linear relation to nutrient concentrations will provide the “best case scenario” for macrophyte concentrations in stream. This method assumes that macrophytes receive nearly all of their nutrients from the water column, so a decrease in concentration will have a similar decrease in macrophyte density. Since macrophyte are able to absorb nutrients from the soils this estimation predicts less macrophytes than what should be observed. The actual optimal nutrient concentrations should lie somewhere between the constant density and linear-related density approximations. Since the constant macrophyte density method did not produce any useable results, the TMDL data will be estimated using only the linear reduction estimation.

In order to keep Silver Bow Creek dissolved oxygen above hypoxic conditions a 50% reduction in nutrients (organic nitrogen, ammonia, nitrate, organic phosphorus, and inorganic phosphorus) and macrophyte density is required.

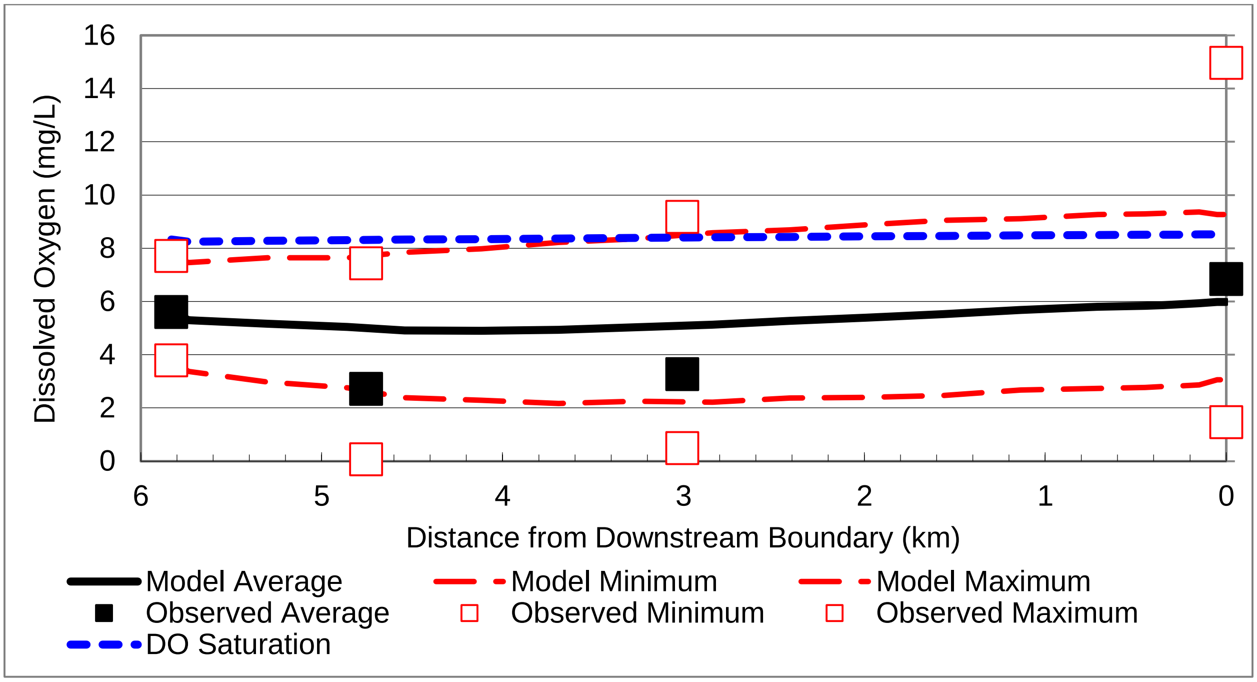

Figure 33: Reduction Required for 2 mg/L Minimum Dissolved Oxygen (50% Reduction)

To ensure Silver Bow Creek stays above 4 mg/L of dissolved oxygen, a 70% reduction of nutrients and macrophytes is required. Stream concentrations are listed in Table XII, and stream loading values are located in Table XIII for both reduction scenarios.

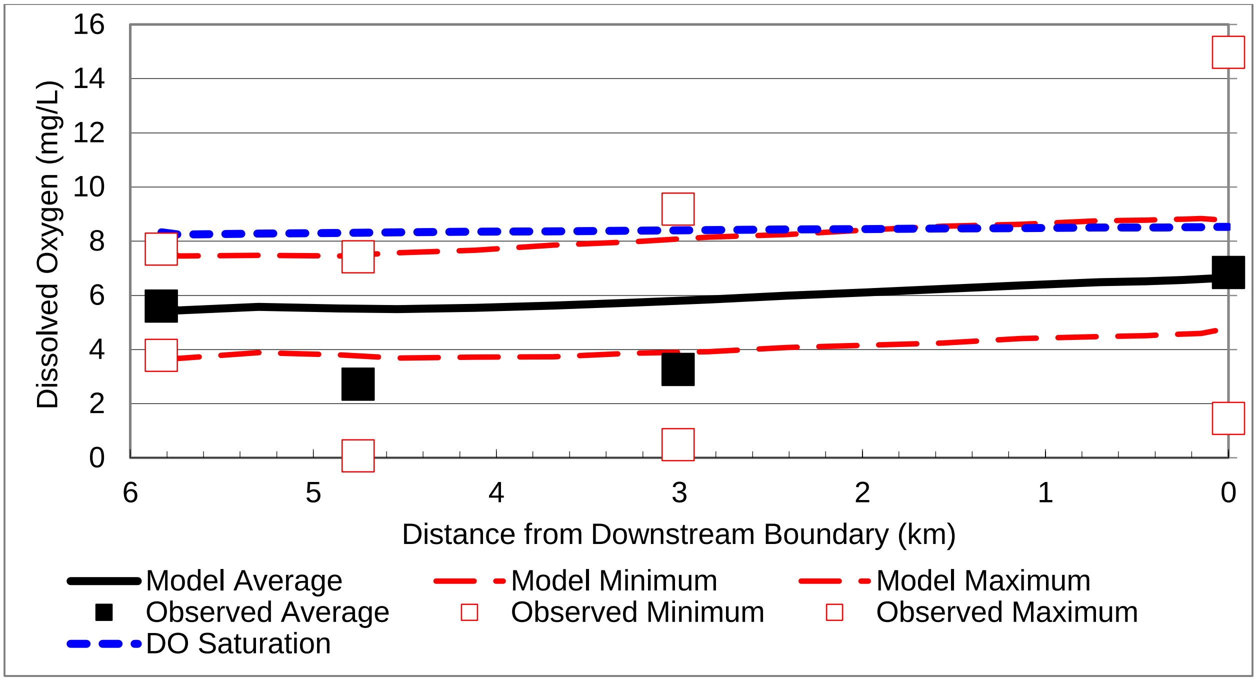

Figure 34: Reduction Required for 4 mg/L Minimum Dissolved Oxygen (70% reduction)

Table XII: Model Parameter Concentrations for Dissolved Oxygen Minimums

Parameter	Initial Concentrations	Concentration to meet 2 mg/L DO	Concentration to meet 4 mg/L DO
Organic Nitrogen	4890 µg/L	2445 µg/L	1467 µg/L
NH_4	7950 µg/L	3975 µg/L	2385 µg/L
NO_3	2025 µg/L	1012 µg/L	607.5 µg/L
Organic Phosphorus	5660 µg/L	2830 µg/L	1698 µg/L
Inorganic Phosphorus	1240 µg/L	620 µg/L	372 µg/L
Point Source DO Mean	-2000 mg/L	-1000 mg/L	-600 mg/L
Point Source DO Range	12000 mg/L	6000 mg/L	3600 mg/L

Table XIII: Stream Loading Values

Parameter	Initial Loading (lb/day)	Loading to meet 2 mg/L DO (lb/day)	Loading to meet 4 mg/L DO (lb/day)
Organic Nitrogen	364	182	109
NH_4	592	296	178
NO_3	151	75	45
Organic Phosphorus	421	211	126
Inorganic Phosphorus	92	46	26

5. Conclusion

The use of point sources in QUAL2K to approximate the effects of macrophytes on a stream appears suitable for dissolved oxygen, temperature, conductivity, and alkalinity outputs. With the exception of dissolved oxygen the remaining parameters are impacted little by the presence of macrophytes. It is difficult to know for certain if the dissolved oxygen approximation is accurate until tests to estimate the production and consumption rates of macrophytes are performed.

5.1. Total Maximum Daily Loading (TMDL)

Current macrophyte biomass, and associated DO source/sink, appear to be large enough to create hypoxic conditions on their own. However it is unlikely that the macrophytes will retain their current loading after the reduction of nutrient loading. Assuming that macrophyte density and nutrient loads are linearly related, it is possible to meet minimum dissolved oxygen standards for fish after their early life stages. A 50% reduction in nutrient and macrophyte loading should prevent dissolved oxygen concentrations falling below 2 mg/L, ensuring the stream is not hypoxic to less mobile species within the reach. A 70% reduction in nutrient and macrophyte density should keep the stream above 4 mg/L, which should be able to sustain fish after their early life cycle. If the macrophyte biomass does not decrease proportionally to the nutrient loading, then a larger amount of nutrients would have to be removed from the stream to keep dissolved oxygen above critical levels.

5.2. Model Improvement and Future Research

Ultimately this project shows how complex the effects of macrophytes are on the stream water quality. Currently QUAL2K is inadequate for modeling large concentrations of macrophytes in stream, but contains all of the necessary tools to make approximations. With additional data collection it would be possible to define the effects of macrophytes on streams and incorporate the macrophytes into the QUAL2K model as their own state-variable. In-situ or bench scale tests should be performed that determine the effects macrophytes have on nutrients, dissolved oxygen, pH, alkalinity, detritus, settling rates, and stream parameters. These results could be incorporated by the addition of another tab that impacts the mass balance equations according to macrophyte demands. Ideally the model would use the existing rate equations, temperature estimations, and fundamental calculations but either include hourly demands of macrophytes, similar to the headwater tab, or a more complex model that predicts nutrient uptake based on the stream conditions.

Twenty four-hour in-situ or bench scale testing could characterize the necessary demand at specific portions along a reach where macrophytes are problematic. By adding other variables to tabs that already exist in a logical order, the model would have a better method to account for large macrophyte concentrations. In-situ tests have the benefit of not needing to relate every parameter to each specific macrophyte, or mixture of macrophytes, and instead just characterizing the effects on the stream. This would provide an excellent, short term approximation of the stream water quality.

A more preferable, longer method would be to create small models that predict macrophyte growth, maximum macrophyte loading, consumption of nutrients per loading, photosynthesis effects on pH, and effects on hydraulics. Since things like photosynthesis and nitrate uptake are related to light intensity, a correlation between these variables would allow the model to predict concentrations more accurately for different weather conditions (Feijoo, Garcia, Momo, & Toja, 2002). Large amounts of photosynthesis will also impact the pH of the stream, so knowing the photosynthetic rate should allow for a more accurate pH estimation. Currently the point source estimation uses a sine curve approximation for diel changes, which isn't fully representative of the diel photosynthetic activity. At the time of the model there was almost 16 hours of daylight, and 8 hours of night, with the sine curve approximating 12 hours of each and underrepresenting the actual contribution of macrophytes.

The model could also be improved by extending the study reach to above the WWTP outfall and into Blacktail Creek, and below the downstream boundary to where the macrophytes are no longer present in the stream or until dissolved oxygen concentrations return to acceptable levels. This will allow for more accurate predictions for water quality based on the background nutrient concentrations from Blacktail Creek and to more accurately define what the WWTP can discharge without negatively impacting dissolved oxygen.

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This is to certify that the thesis prepared by Dylan Uecker entitled "Application of QUAL2K Model to Macrophyte Rich Silver Bow Creek" has been examined and approved for acceptance by the Department of Environmental Engineering, Montana Tech of The University of Montana, on this 28th day of April, 2016.

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